PB82-249202

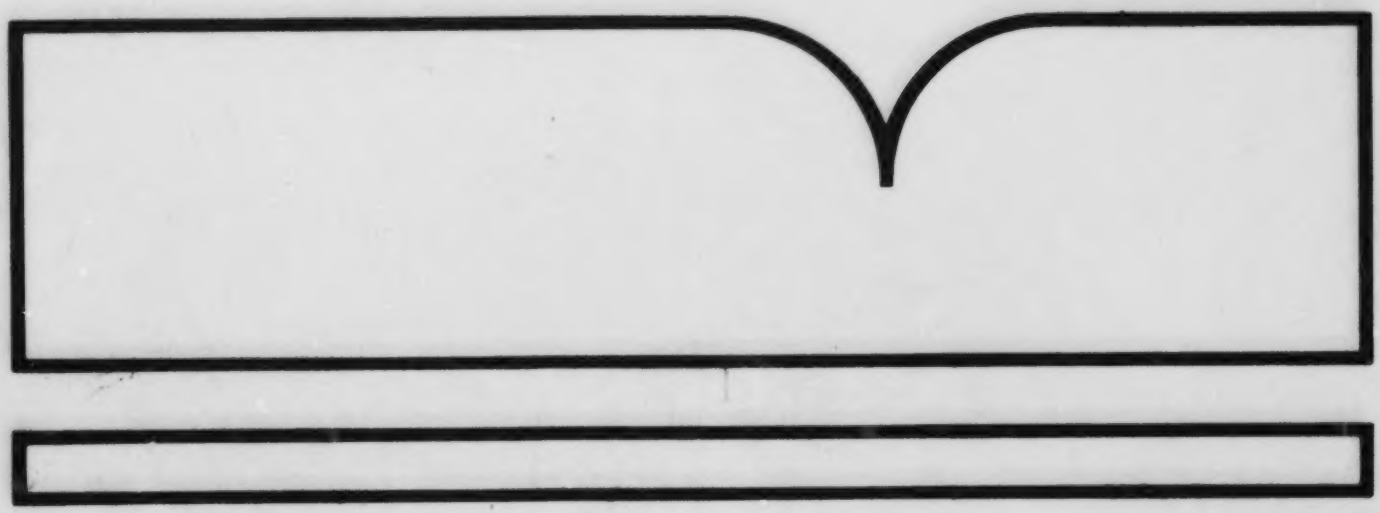
Trace Chemical in the 'Clean' Troposphere

SRI International
Menlo Park, CA

Prepared for

Environmental Sciences Research Lab.
Research Triangle Park, NC

Oct 81



U.S. Department of Commerce
National Technical Information Service
NTIS

EPA-600/3-81-055
October 1981

PB82-249202

TRACE CHEMICAL IN THE "CLEAN" TROPOSPHERE

by

H.B. Singh, L.J. Salas, and R. Stiles
Atmospheric Science Center
SRI International
333 Ravenswood Avenue
Menlo Park, California 94025

Grant No. R806729

Project Officer

Bruce W. Gay, Jr.
Atmospheric Chemistry and Physics Division
Environmental Sciences Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

ENVIRONMENTAL SCIENCES RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/3-81-055	2.
3. RECIPIENT'S ACCESSION NO. PB82 249202	
4. TITLE AND SUBTITLE TRACE CHEMICALS IN THE "CLEAN" TROPOSPHERE	5. REPORT DATE October 1981
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Singh, H.B., L. J. Salas, R. Stiles	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS SRI International 333 Ravenswood Avenue Menlo Park, California 94025	10. PROGRAM ELEMENT NO. CCUL1A/04 0515 (FY-81)
	11. CONTRACT/GRANT NO. R806729
12. SPONSORING AGENCY NAME AND ADDRESS Environmental Sciences Research Laboratory-RTP, NC Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, North Carolina 27711	13. TYPE OF REPORT AND PERIOD COVERED Interim 1979-1980
	14. SPONSORING AGENCY CODE EPA/600/09

15. SUPPLEMENTARY NOTES

16. ABSTRACT

Atmospheric measurements at Point Arena, California (39°N) are used to assess the burden as well as the growth rates of a large number of important atmospheric trace chemicals. In early 1981 the organic fluorine, chlorine, bromine, and iodine burden of the northern hemisphere (midlatitudes) was determined to be 1.3 parts per billion (ppb), 3.7 ppb, 0.02 ppb, and less than 0.003 ppb respectively. An increase of approximately 25 percent in the atmospheric burden of fluorine and chlorine appears to have occurred over the last three years. Nearly 80 percent of chlorine atoms and 100 percent of fluorine atoms are attributable to man-made sources. No changes appear to be occurring in the bromine and iodine burdens; however, their concentrations are much lower and less well characterized. The atmospheric growth rate of nitrous oxide is immeasurably small (less ± 2 ppb per year). Fluorocarbon 12, fluorocarbon 11, carbon tetrachloride, and methyl chloroform are measured to be increasing during the period of this study (December 1979 to February 1981) at an average rate of 25 parts per trillion (ppt) per year, 19 ppt per year, 5 ppt per year and 18 ppt per year respectively. The dominant natural halocarbon, methyl chloride, does not appear to show any detectable trends. Among the important man-made chemicals such as methylene chloride, 1,2 dichloroethane, tetrachloroethylene, and trichloroethylene, slightly declining trends or change is evident.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS (This Report) UNCLASSIFIED	21. NO. OF PAGES 57
	20. SECURITY CLASS (This page) UNCLASSIFIED	22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

NOTICE

Mention of trade names or commercial products does not consititute endorsement or recommendation for use.

ABSTRACT

Our atmospheric measurements at Point Arena, California ($39^{o}N$) are used to assess the burden as well as the growth rates of a large number of important atmospheric trace chemicals. In early 1981 the organic fluorine, chlorine, bromine, and iodine burden of the northern hemisphere (midlatitudes) was determined to be 1.3 parts per billion (ppb), 3.7 ppb, 0.02 ppb, and <0.003 ppb respectively. An increase of approximately 25 percent in the atmospheric burden of fluorine and chlorine appears to have occurred over the last three years. Nearly 80 percent of chlorine atoms and 100 percent of fluorine atoms are attributable to man-made sources. No changes appear to be occurring in the bromine and iodine burdens, however, these concentrations are much lower and are less well characterized.

The atmospheric growth rate of nitrous oxide is immeasurably small (<± 2 ppb per year). Fluorocarbon 12, fluorocarbon 11, carbon tetrachloride, and methyl chloroform are measured to be increasing during the period of this study (December 1979 to February 1981) at an average rate of 25 parts per trillion (ppt) per year, 19 ppt per year, 5 ppt per year and 18 ppt per year respectively. The dominant natural halocarbon, methyl chloride, does not appear to show any detectable trends. Among the important man-made chemicals such as methylene chloride, 1,2 dichloroethane, tetrachloroethylene, and trichloroethylene, slightly declining trends or no change is evident.

Analysis of the fate of atmospheric nonmethane hydrocarbons (largely ethane and propane) is performed to suggest the hitherto unrecognized role of reactive organic nitrogen in the troposphere and the stratosphere. It is shown that more than half the reactive nitrogen in the troposphere may exist in its combined organic form.

This is an interim progress report in partial fulfullment of the U.S. Environmental Protection Agency Grant R806 729.

CONTENTS

ABSTRACT..... iii

LIST OF FIGURES..... vi

LIST OF TABLES..... vii

1 INTRODUCTION..... 1

2 OVERALL OBJECTIVES..... 3

3 ANALYTICAL METHODOLOGY..... 4

Calibration Standards..... 6
Quality Control..... 9

4 ANALYSIS OF FIELD DATA..... 12

Nitrous Oxide..... 12
Fluorocarbons..... 15
Halomethanes..... 17
Haloethanes..... 21
Chloroethylenes..... 25
Nonmethane Hydrocarbons..... 25

5 FORMATION OF SECONDARY PRODUCTS FROM GLOBALLY DISTRIBUTED TRACE CHEMICALS..... 28

Analysis..... 28
Results and Discussion..... 35

6 SUMMARY OF RESULTS..... 39

7 FUTURE PLANS..... 43

REFERENCES..... 44

FIGURES

Number		Page
1	Specially Treated 1-Liter Stanless-Steel Sampling Vessel for Collecting Grab Samples	5
2	Permeation Tube Weight-Time Relationship for Selected Chemicals	8
3	Nitrous Oxide Concentration Versus Days (Day 1 is 721206)	15
4	Fluorocarbon 12 Concentration Versus Days	16
5	Fluorocarbon 11 Concentration Versus Days	16
6	Fluorocarbon 113 Concentration Versus Days	18
7	Fluorocarbon 114 Concentration Versus Days	18
8	Methyl Chloride Concentration Versus Days	19
9	Methyl Bromide Concentration Versus Days	19
10	Methyl Iodide Concentration Versus Days	20
11	Methylene Chloride Concentration Versus Days	20
12	Choloroform Concentration Versus Days	22
13	Carbon Tetrachloride Concentration Versus Days	22
14	Ethyl Chloride Concentration Versus Days	23
15	1,2 Dichloroethane Concentration Versus Days	23
16	1,2 Dibromethane Concentration Versus Days	24
17	1,1,1 Trichloroethane Concentration Versus Days	24
18	Trichloroethylene Concentration Versus Days	26
19	Tetrachloroethylene Concentration Versus Days	26
20	Ethane Concentration Versus Days	27
21	A Schematic of the PAN and Acetaldehyde Profile in the Atmosphere	37

TABLES

Number		Page
1	Permeation-Rate Data for Generating Primary Standards.....	7
2	PPM-Level Primary Standards in Air.....	10
3	Interlaboratory Comparison of Selected Trace Constituents.....	11
4	Measurement of Trace Constituents at Point Arena--Field Studies 1-8.....	13
5	Measurement of Trace Constituents at Point Arena--Field Studies 9-17.....	14
6	Atmospheric Abundance of Trace Species of Interest at Selected Elevations.....	29
7	List of Rate Constants Used in this Study.....	31
8	Estimated Concentration of Acetaldehyde, Acetone, and PAN.....	36
9	Average Background Concentrations of Important Trace Chemicals in the Northern Hemisphere (40^{o}N).....	40
10	Average Atmospheric Growth Rates of Selected Species from Late 1979 to Early 1981 in the Northern Hemisphere (40^{o}N).....	41
11	Tropospheric Chlorine, Bromine, Iodine, and Fluorine Organic Budgets for Early 1981 in the Northern Hemisphere (40^{o}N).....	41

SECTION 1

INTRODUCTION

Over the last decade, an increasing number of hazardous chemicals have been released into the environment. Many halocarbon species that are stable in the troposphere (such as chlorofluorocarbons and carbon tetrachloride) are suspect as precursors of stratospheric ozone-destroying chlorine atoms. Other chloromethanes (such as $CHCl_3$ and CCl_4) and chloroethylenes (C_2HCl_3 and C_2Cl_4) are feared to be carcinogenic. Several halocarbons as well as hydrocarbons and N_2O absorb infrared heat radiation and could exacerbate the atmospheric warming caused by CO_2. In addition, many of these chemicals are oxidized in the atmosphere to form products that play an important role in the chemistry of the atmosphere. The protection of our global environment requires a closer inspection of the growth of hazardous chemicals in the troposphere.

This ongoing study is intended to characterize the long-term variabilities and changes in the atmospheric abundance of a large number of natural and man-made trace constituents. In addition to being a valuable source of knowledge about the fundamental behavior of the natural atmosphere, long-term measurements of important trace constituents are an essential means of projecting future effects and determining whether existing strategies are working. Furthermore, collecting such data is a necessary step in establishing the sources and sinks of atmospheric trace constituents. Experimental data are being complemented by theoretical analysis to postulate the fates of these chemicals and the importance of their secondary products.

The present long-term measurements are primarily designed to answer the following questions:

- What is the tropospheric burden of selected trace constituents and how does it change with time?
- What are the residence times, sources, sinks, and fates of these pollutants?
- What is the nature and role of important secondary products?

SECTION 2

OVERALL OBJECTIVE

The overall objectives of this study are to

- Obtain highly accurate and precise, internally consistent, long-term atmospheric measurements to characterize better the abundance and temporal variability of a comprehensive group of selected trace chemicals.
- Analyze data collected during this study and integrate it with data acquired from outside sources.
- Assess the nature and the role of secondary products in the chemistry of the troposphere and the stratosphere.

SECTION 3

ANALYTICAL METHODOLOGY

The sampling location chosen for this study is Point Arena, California, 38°57'N, 123°44'W, roughly 150 miles from SRI's headquarters. This is a clean marine Pacific Coast site, especially under conditions of westerly air flows. Climatological data indicate that this is the case during most of the year except the winter months. The Point Arena Coast Guard station has been frequently consulted to preselect sampling days.

The air samples were collected at Point Arena between 1200 and 1500 local time. During this time, a strong sea breeze is prevalent; therefore it seemed that samples collected during these hours would be least affected by continental anthropogenic pollution. Samples were taken in 1-l electropolished stainless-steel canisters (Figure 1), pressurized at 35 to 40 psig. The canisters were precleaned at 100°C by flushing them with cryogenically cleaned ultra-pure air and then testing them for cleanliness. Four to ten air samples were collected during a typical sampling trip. It was felt that a minimum of four samples was necessary to establish the average air concentration.

The samples were transported to SRI's central laboratories and analyzed within two to three days. The analysis procedures have been described before and need not be repeated here (Singh et al., 1979a, 1980).* In general, cryogenic preconcentration techniques at liquid O_2 temperature were used with

*References are listed at the end of the report.

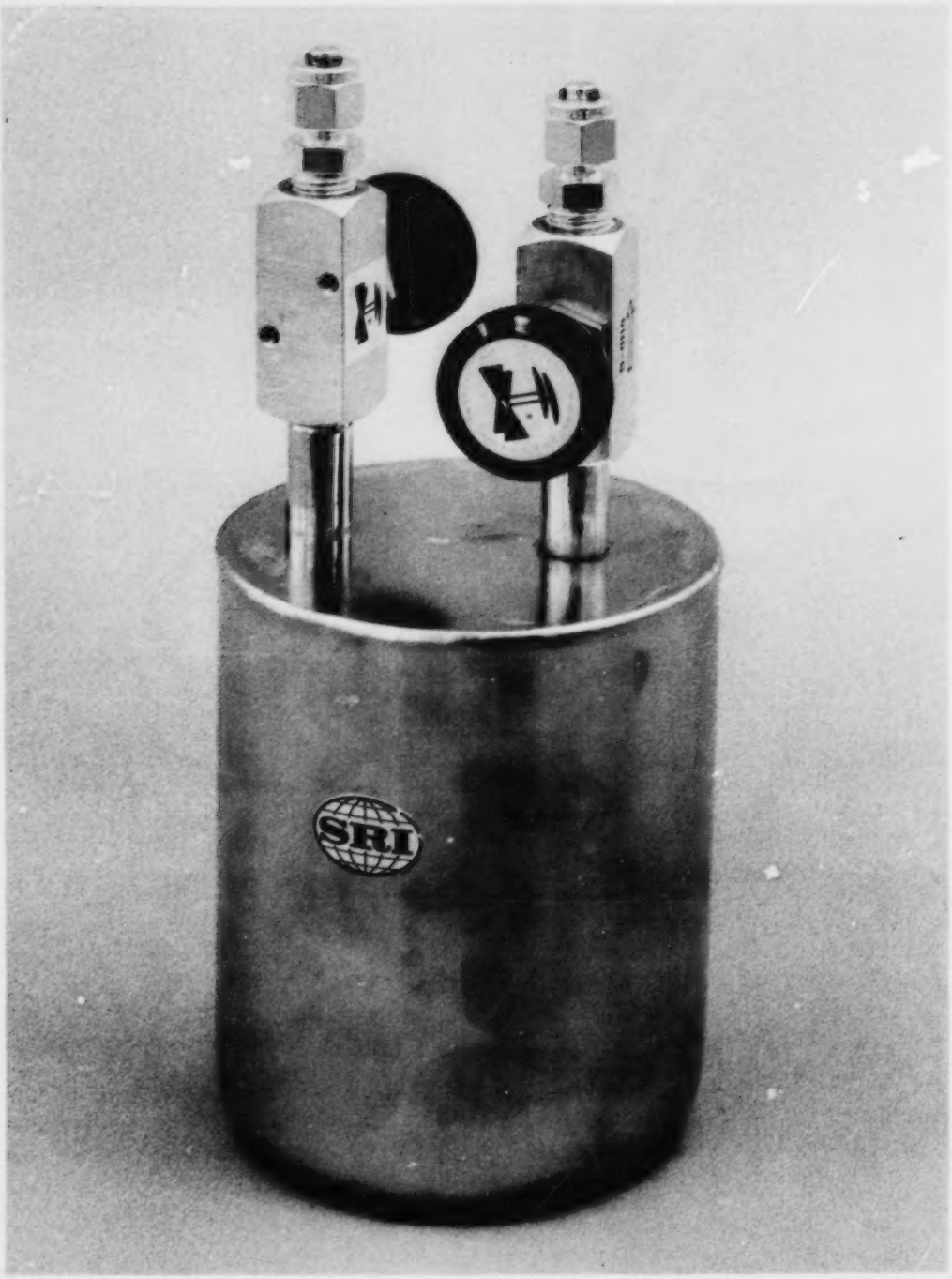


FIGURE 1 SPECIALLY TREATED 1-LITER STAINLESS-STEEL SAMPLING VESSEL FOR COLLECTING GRAB SAMPLES

freezeout traps containing SE-30 or glass wool. For some species (such as N_2O) a direct 5-ml injection with a sampling loop provided the greatest precision and was therefore used.

CALIBRATION STANDARDS

At the beginning of this study, three electropolished stainless steel canisters of 35-l volume (specially constructed for this project) each were filled to 40 psi with the Point Arena air. These large cylinders were used as secondary standards. Each contained enough air for the entire three-year study. During analysis of air samples, secondary standards were injected at the rate of once per every three samples analyzed, at a minimum. For N_2O, the secondary standards were analyzed with every air sample.

As reported earlier (Singh et al., 1979a; 1980), permeation tubes provide the best way of generating low-ppb primary standards for a significant number of chemicals under study. (Previously these were unaceptable for a number of species.) Based on our experience, we concluded that unacceptable permeation tubes could operate satisfactorily at high temperatures. Therefore two temperature baths maintained at 30.0 $\pm$0.05°C and 70 $\pm$0.1°C were installed. The 30°C bath was a water bath and the 70°C bath was an oil bath. All permeation tubes were contained in specialized holders and were purged continuously with a prepurifier gas (He, air, or N_2) flowing at 50 to 80 ml/min. A large-volume mixing chamber was installed at the permeation tube exit to allow for complete mixing. All-glass syringes were used to withdraw samples from the mixing chamber. When the the 70°C bath was installed, all permeation tubes performed excellently. Table 1 reports the measured permeation-rate data for each of the chemical constituents of interest. It is clear from the table that many species for which permeation tubes could not be used earlier (such as CCl_4, CH_3CCl_3, CH_2BrCH_2Br, and chloroaromatics) are now giving highly dependable results. Figure 2 demonstrates the excellent linearity of the permeation rate for some of these chemicals. Overall, we believe that this offers the best, most accurate means of generating primary standards.

Table 1

PERMEATION-RATE DATA FOR GENERATING PRIMARY STANDARDS

Compound	Permeation Tube Number or I.D.	Temperature, (°C*)	Permeation Rate		Status†	Quality†
			ng/min	ppb/l/min (25°C, 1 atm)		
CH_2=CHCHO	2356	30.0	969	423	S	E
CH_2OCH_2	1908	30.0	1120	618	S	E
CCl_2F_2 (F12)	6138	30.0	615	123	S	E
CCl_3F (F11)	1911	30.0	1680	299	S	E
$CHCl_2F$ (F21)	2347	30.0	942	224	S	E
$CHClF_2$ (F22)	2348	30.0	80	23	?	E
CCl_2FCClF_2 (F113)	1238	30.0	715	93	S	E
$CClF_2CClF_2$ (F114)	2345	30.0	6254	894	S	E
CH_3Cl	2355	30.0	1915	927	S	E
C_2H_5Cl	2350	30.0	480	182	S	E
CH_2CHCl	2352	30.0	1270	497	S	E
$ClCH_2CH$=CH_2	7497	30.0	142	45	S	E
CH_3Br	1893	30.0	2477	638	S	G
CH_3I	1239	30.0	109	19	S	G
CH_2Cl_2	2354	30.0	523	150	S	E
(cis) CHClCHCl	1939	30.0	2564	646	S	G
(trans) CHClCHCl	1898	30.0	1696	428	S	G
CCl_2CH_2	1897	30.0	731	184	S	G
CH_2ClCH_2Cl	1907	70.0	2622	648	S	E
CH_2ClCH_2Cl	1899	30.0	125	31	S	G
$CHCl_2CH_3$	2353	30.0	71	18	S	G
$CH_2ClCHClCH_3$	MET1	70.0	2456	531	S	E
(trans) CHCl=$CHCH_2Cl$	MET2	70.0	7806	1720	S	E
$COCl_2$	2351	30.0	942	233	S	E
$CHCl_3$	1229	30.0	174	36	S	G
C_2HCl_3	1235	30.0	314	58	S	E
CCl_3CH_3	1896	70.0	980	179	S	E
CCl_3CH_3	1589	70.0	3450	632	S	E
$CHCl_2CH_2Cl$	1901	30.0	129	24	S	G
CCl_4	1894	70.0	1983	315	S	E
C_2Cl_4	1902	70.0	3352	494	S	E
C_2Cl_4	1590	30.0	706	104	S	E
CH_2BrCH_2Br	1237	70.0	1220	160	S	E
$CHBr_3$	1895	70.0	1316	127	S	E
C_6H_5Cl	MET3	70.0	4507	980	S	E
$C_6H_5CH_2Cl$	MET4	70.0	1528	295	S	E
o-$C_6H_4Cl_2$	MET5	70.0	1359	226	S	E
m-$C_6H_4Cl_2$	MET6	70.0	2515	418	S	E
p-$C_6H_4Cl_2$	MET7	70.0	1596	265	S	E

NOTE: All permeation tubes were given a 2 week or longer conditioning time

*Temperature maintained to ± 0.05°C

†E–Excellent (errors in permeation rate < ±10%); G–Good (errors in permeation rate < ±15%); S–Satisfactory (< ±19%)

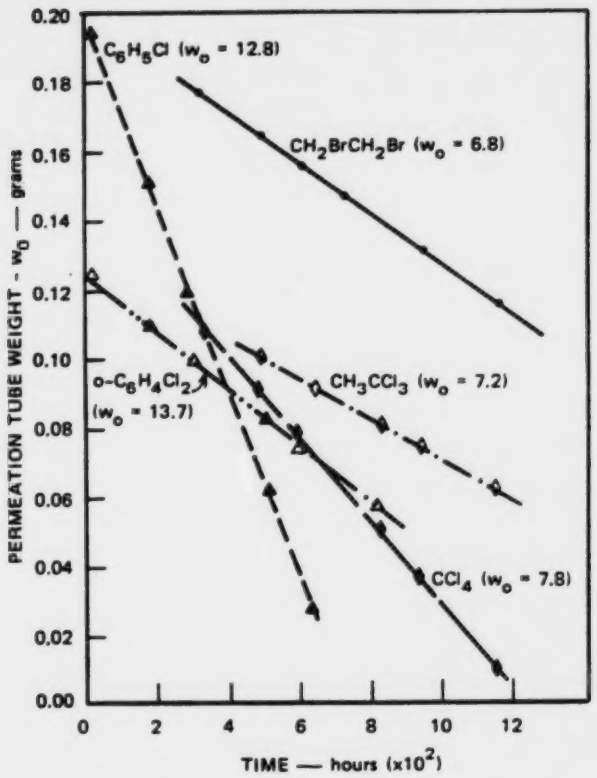


FIGURE 2 PERMEATION TUBE WEIGHT-TIME RELATIONSHIP FOR SELECTED CHEMICALS

It is also clear from Table 1 that most of these permeation tubes can be used to prepare standards directly at parts per billion (ppb) concentration levels. Batch dilutions were carried out to reduce these concentrations by a factor of 10^2 to 10^3. Over a wide range of concentration levels of several ppb's and low ppt's, the frequency-modulated Electron Capture Detectors (ECDs) that we used were completely linear. The linearity of the Flame Ionization Detector (FID) over a much larger concentration range is well known.

In addition to permeation tubes, standards were obtained from Scott-Marrin, Inc. (Riverside, California). These were of higher concentrations (5 to 10 ppm) for long-term stability. Table 2 lists the chemicals, the standard concentrations, and the cylinder materials. All of the chemicals were stored in aluminum cylinders except CH_3Cl, which was in stainless-steel cylinders. Extreme care was required in selecting cylinder materials, since some of the chemicals (such as CH_3Cl) form unknown chemical complexes and could lead to potentially explosive conditions with aluminum. Static dilution systems were devised to reduce ppm concentrations to ppt levels. Both the ECD (frequency modulated) and the FID were found to be highly linear in the ppb to ppt concentration range.

All of the commercially obtained standards were rechecked with our permeation-tube standards whenever possible. The comparisons were found to yield excellent results (±10 percent). The hydrocarbon standards were checked for carbon response against those available from the National Bureau of Standards (NBS) and were found to agree to within ±5 percent.

QUALITY CONTROL

Two major factors were critical in establishing the quality of the acquired data: the accuracy of the primary standards, and the precision and repeatability of measurements. As stated earler in this section, the primary standards commercially obtained were compared with our permeation tubes, which can routinely be used to obtain reliable standards within an error range of ±5 to 10 percent. The aromatic hydrocarbon standards were compared with NBS propane standards and found to be accurate to within ±5 percent. The cross-calibrations between SRI-generated standards and Scott-Marrin standards

Table 2

PPM-LEVEL PRIMARY STANDARDS IN AIR*

Standard and Compound†	Concentration (ppm)	Long-Term Stability‡ (1-year period)	Cylinder	
			Type	Size (ft^3)
S1				
1,1,1 Trichloroethane	5.0	E		
Carbon tetrachloride	5.2	P	Aluminum	30
1,2 Dibromoethane	5.0	E		
Hexachloroethane	0.8	U		
S2				
Ethane	4.07	E		
Propane	5.03	E	Aluminum	150
n-Butane	4.95	E		
S3				
Benzene	5.0	E	Aluminum	150
Toluene	5.0	E		
S4				
Methyl chloride	10.0	E		
Methylene chloride	10.0	E	Stainless steel	30
1,2 Dichloroethane	10.0	E		
S5				
Trichloroethylene	10.0	E		
Tetrachloroethylene	10.0	E	Aluminum	30
Chloroform	10.0	E		

*Obtained on order from Scott-Marrin, Inc., Riverside, California.

†For all of these chemicals (except hydrocarbon) satisfactory permeation tubes were also operational. Therefore, a majority of these standards were used more as secondary standards than as primary ones. The Scott-Marrin standards were used as primary standards.

‡E: excellent; P: poor; U: unknown.

typically result in differences of about ±10 percent or less. The use of secondary standards nearly three times a day clearly demonstrated the excellent precision that was obtainable during field studies. The precision of reported field measurements is estimated to be ±5 percent. The measurements presented here have an overall estimated accuracy of better than ±15 percent. The difficulties in storing long-term secondary standards are considerable, and often one has to resort to primary standards. Thus the ability to regenerate accurate primary standards repeatedly is essential to the success of such a program of long-term measurements. Table 3 shows the results of an interlaboratory comparison of samples. For all species, the comparison appears to be valid to ±5 percent, except for N_2O, where the difference is closer to ±8 percent.

Table 3

INTERLABORATORY COMPARISON OF SELECTED TRACE CONSTITUENTS

Chemicals	Sample 1		Sample 2	
	SRI*	OGC†	SRI*	OGC†
N_2O	312 ppb	336 ppb	309 ppb	335 ppb
CCl_2F_2	315 ppt	330 ppt	285 ppt	298 ppt
CCl_3F	280 ppt	278 ppt	175 ppt	175 ppt
CH_3CCl_3	180 ppt	183 ppt	131 ppt	138 ppt

*Samples of unknown composition ("blind samples") analyzed at SRI.

†Same samples analyzed by Oregon Graduate Center (OGC).

SECTION 4

ANALYSIS OF FIELD DATA

In general, experiments have proceeded satisfactorily. Despite occasional contamination of specific chemicals, the data collected appear to be fairly representative of clean tropospheric conditions. Tables 4 and 5 show the results obtained during our field studies conducted between December 1979 and February 1981. Additional measurements are continuing. The average concentration of each chemical and the corresponding standard deviation are shown in the table. In the following sections, data presented in the table will be briefly interpreted and discussed.

NITROUS OXIDE

Nitrous oxide (N_2O) was measured at an average concentration of 310 to 316 ppb (Tables 4 and 5). The data are plotted in Figure 3. The broken line is a least-squares regression line through the mean data. It is obvious from Figure 3 that there was no significant change in the mean atmospheric abundance of N_2O during the period of our observations. Little change in N_2O concentration is evident when we compare these data with our 1978 values (Singh et al., 1979a). A recent report by Weiss (1981) suggests that over the last decade N_2O may have increased at a rate of about 0.2 percent per year. All these findings are consistent with the view that denitrification of nitrogen fertilizer is perturbing atmospheric N_2O at a rate far slower than predicted by modelers (N_2O increases as high as 4 percent per year have been predicted). Consistent with the atmosphere behavior of long-lived species, the variabilities of N_2O are small (σ = 0.3 to 2 percent).

Table 4

MEASUREMENT OF TRACE CONSTITUENTS AT POINT ARENA--FIELD STUDIES 1-8

Compound (units)*	Field Study							
	1 (08 Dec 79)	2 (26 Jan 80)	3 (10 Apr 80)	4 (20 Apr 80)	5 (05 May 80)	6 (09 Aug 80)	7 (13 Aug 80)	8 (24 Sep 80)
N_2O (ppb)	312 ± 1	311 ± 3	314 ± 1	314 ± 4	311 ± 4	314 ± 1	315 ± 1	316 ± 2
CCl_2F_2 (ppt)	273 ± 14	277 ± 17	293 ± 17	470 ± 94	290 ± 13	283 ± 6	288 ± 6	288 ± 6
CCl_3F (ppt)	173 ± 4	170 ± 5	163 ± 2	224 ± 3	183 ± 7	179 ± 5	178 ± 2	181 ± 4
CCl_2FCClF_2 (ppt)	31 ± 3	27 ± 5	28 ± 3	137 ± 24	33 ± 5	40 ± 16	55 ± 11	24 ± 4
$CClF_2CClF_2$ (ppt)	14 ± 2	13 ± 2	16 ± 2	19 ± 2	23 ± 5	15 ± 2	19 ± 6	12 ± 1
CH_3Cl (ppt)	753 ± 27	681 ± 84	765 ± 66	828 ± 188	792 ± 128	773 ± 40	796 ± 33	682 ± 112
CH_3Br (ppt)	3 ± 1	7 ± 1	12 ± 2	9 ± 3	7 ± 1	10 ± 1	20 ± 5	15 ± 5
CH_3I (ppt)	5 ± 2	7 ± 2	4 ± 1	4 ± 1	5 ± 1	4 ± 0	6 ± 2	5 ± 0
CH_2Cl_2 (ppt)	41 ± 6	45 ± 3	53 ± 7	55 ± 18	53 ± 10	50 ± 7	88 ± 27	36 ± 3
$CHCl_3$ (ppt)	23 ± 2	18 ± 2	20 ± 1	17 ± 2	18 ± 3	27 ± 1	32 ± 9	24 ± 2
CCl_4 (ppt)	113 ± 7	135 ± 9	135 ± 2	130 ± 4	133 ± 6	151 ± 17	129 ± 6	137 ± 1
C_2H_5Cl (ppt)	–	–	–	–	–	–	–	11 ± 2
CH_2ClCH_2Cl (ppt)	–	–	–	–	–	–	–	48 ± 5
CH_2BrCH_2Br (ppt)	8 ± 2	5 ± 3	6 ± 2	5 ± 3	7 ± 1	6 ± 1	9 ± 4	2 ± 1
CH_3CCl_3 (ppt)	153 ± 10	161 ± 9	174 ± 13	177 ± 19	159 ± 16	162 ± 9	170 ± 10	170 ± 4
C_2HCl_3 (ppt)	21 ± 2	19 ± 3	15 ± 3	11 ± 3	12 ± 3	19 ± 3	25 ± 4	25 ± 14
C_2Cl_4 (ppt)	53 ± 9	45 ± 3	49 ± 5	124 ± 25	93 ± 6	50 ± 9	42 ± 7	48 ± 6
C_2H_2 (ppb)	–	–	0.21 ± 0.01	0.71 ± 0.06	0.88 ± 0.04	–	–	0.47 ± 0.05
C_2H_4 (ppb)	–	0.36 ± 0.05	0.35 ± 0.05	2.52 ± 0.05	2.48 ± 0.26	–	–	–
C_2H_6 (ppb)	2.01 ± 0.16	2.31 ± 0.28	4.04 ± 0.52	2.29 ± 0.14	2.63 ± 0.34	–	–	1.27 ± 0.17
C_3H_8 (ppb)	–	0.56 ± 0.12	0.89 ± 0.10	0.35 ± 0.04	–	0.40 ± 0.02	0.35 ± 0.00	0.51 ± 0.11
$I\text{-}C_4H_{10}$	–	–	–	–	–	–	–	–
$N\text{-}C_4H_{10}$	–	–	–	–	–	0.53 ± 0.05	0.25 ± 0.02	0.26 ± 0.15

*ppt = 10^{-12} v/v; ppb = 10^{-9} v/v

Table 5

MEASUREMENT OF TRACE CONSTITUENTS AT POINT ARENA--FIELD STUDIES 9-17

Compound (units)*	Field Study								
	9 (29 Sep 80)	10 (12 Nov 80)	11 (13 Dec 80)	12 (08 Jan 81)	13 (15 Jan 81)	14 (24 Jan 81)	15 (30 Jan 81)	16 (06 Feb 81)	17 (18 Feb 81)
N_2O (ppb)	312 ± 2	314 ± 4	312 ± 4	312 ± 6	312 ± 4	316 ± 2	314 ± 0	313 ± 7	310 ± 3
CCl_2F_2 (ppt)	287 ± 4	293 ± 6	292 ± 4	311 ± 11	315 ± 19	299 ± 6	310 ± 7	302 ± 8	306 ± 7
CCl_3F (ppt)	181 ± 4	183 ± 3	188 ± 5	192 ± 8	190 ± 6	187 ± 7	190 ± 7	191 ± 8	191 ± 7
$CClF_2FCClF_2$ (ppt)	28 ± 6	25 ± 4	24 ± 4	24 ± 4	37 ± 18	28 ± 3	25 ± 4	32 ± 3	33 ± 3
$CClF_2CClF_2$ (ppt)	14 ± 2	13 ± 3	15 ± 1	17 ± 4	13 ± 3	13 ± 3	15 ± 2	15 ± 2	15 ± 5
CH_3Cl (ppt)	676 ± 39	787 ± 74	755 ± 72	777 ± 36	709 ± 172	715 ± 139	898 ± 36	674 ± 56	749 ± 119
CH_3Br (ppt)	14 ± 3	8 ± 0	12 ± 7	14 ± 5	9 ± 1	11 ± 2	11 ± 2	12 ± 0	8 ± 0
CH_3I (ppt)	3 ± 1	3 ± 0	3 ± 0	3 ± 0	3 ± 1	3 ± 2	3 ± 0	3 ± 1	5 ± 1
CH_2Cl_2 (ppt)	39 ± 2	34 ± 3	29 ± 2	67 ± 14	44 ± 13	52 ± 9	36 ± 5	47 ± 7	28 ± 4
$CHCl_3$ (ppt)	14 ± 4	34 ± 2	29 ± 7	18 ± 3	8 ± 3	16 ± 1	12 ± 3	37 ± 5	20 ± 1
CCl_4 (ppt)	139 ± 15	131 ± 12	162 ± 23	140 ± 17	134 ± 7	132 ± 3	136 ± 23	153 ± 15	124 ± 15
C_2H_5Cl (ppt)	22 ± 13	16 ± 3	–	11 ± 5	8 ± 3	16 ± 1	18 ± 1	17 ± 6	4 ± 2
CH_2ClCH_2Cl (ppt)	39 ± 3	53 ± 13	57 ± 11	43 ± 6	43 ± 4	49 ± 2	42 ± 5	43 ± 3	45 ± 4
CH_2BrCH_2Br (ppt)	–	4 ± 1	3 ± 1	3 ± 0	2 ± 0	3 ± 1	2 ± 0	–	–
CH_3CCl_3 (ppt)	176 ± 8	177 ± 6	174 ± 14	182 ± 4	177 ± 7	176 ± 9	177 ± 7	182 ± 12	183 ± 9
C_2HCl_3 (ppt)	13 ± 3	14 ± 4	12 ± 1	19 ± 5	9 ± 1	17 ± 2	18 ± 4	17 ± 1	13 ± 2
C_2Cl_4 (ppt)	37 ± 6	36 ± 5	40 ± 13	104 ± 21	41 ± 4	58 ± 20	51 ± 7	47 ± 13	38 ± 5
C_2H_2 (ppb)	0.28 ± 0	0.66 ± 0.12	0.62 ± 0.07	1.56 ± 0.06	0.64 ± 0.08	0.29 ± 0.06	0.46 ± 0.01	0.48 ± 0.01	0.41 ± 0.11
C_2H_4 (ppb)	–	0.48 ± 0.20	–	0.14 ± 0.02	0.54 ± 0.17	1.72 ± 0.05	0.30 ± 0.03	0.30 ± 0.05	0.16 ± 0.02
C_2H_6 (ppb)	1.55 ± 0.05	1.88 ± 0.32	1.63 ± 0.61	2.43 ± 1.71	1.98 ± 1.62	5.85 ± 0.23	2.14 ± 0.21	2.07 ± 0.24	1.79 ± 0.08
C_3H_8 (ppb)	0.34 ± 0.04	0.88 ± 0.08	0.76 ± 0.20	–	2.29 ± 0.22	1.05 ± 0.01	1.03 ± 0.06	0.94 ± 0.09	0.93 ± 0.08
$I\text{-}C_4H_{10}$	–	0.16 ± 0.02	0.16 ± 0.02	–	0.53 ± 0.09	0.21 ± 0.02	–	0.21 ± 0.00	0.14 ± 0.04
$N\text{-}C_4H_{10}$	0.31 ± 0.17	0.28 ± 0.05	0.31 ± 0.07	–	1.00 ± 0.13	0.43 ± 0.02	0.44 ± 0.03	0.38 ± 0.04	0.22 ± 0.02

*ppt = 10^{-12} v/v; ppb = 10^{-9} v/v

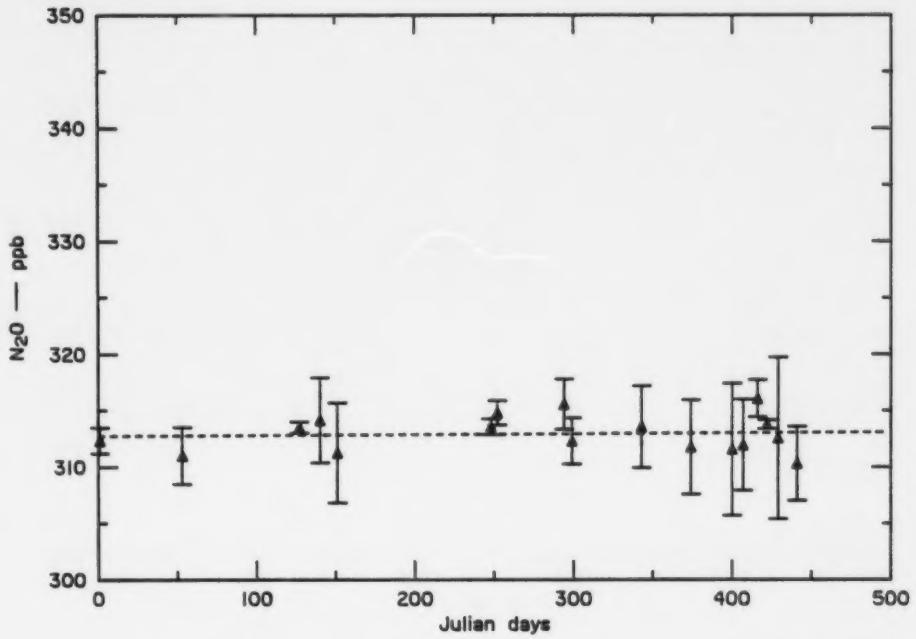
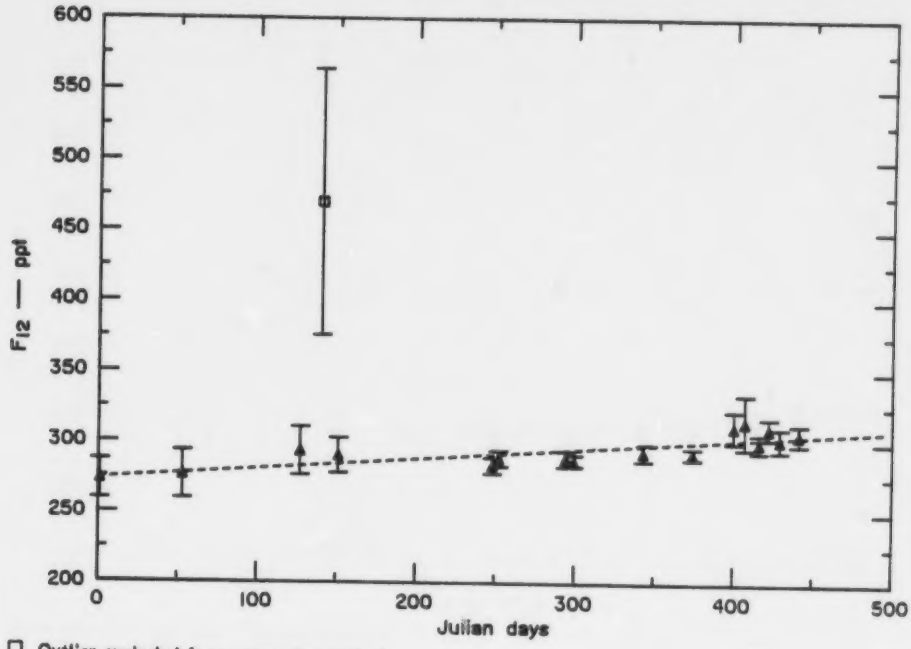


FIGURE 3 NITROUS OXIDE CONCENTRATION VERSUS DAYS (Day 1 is 791206)

FLUOROCARBONS

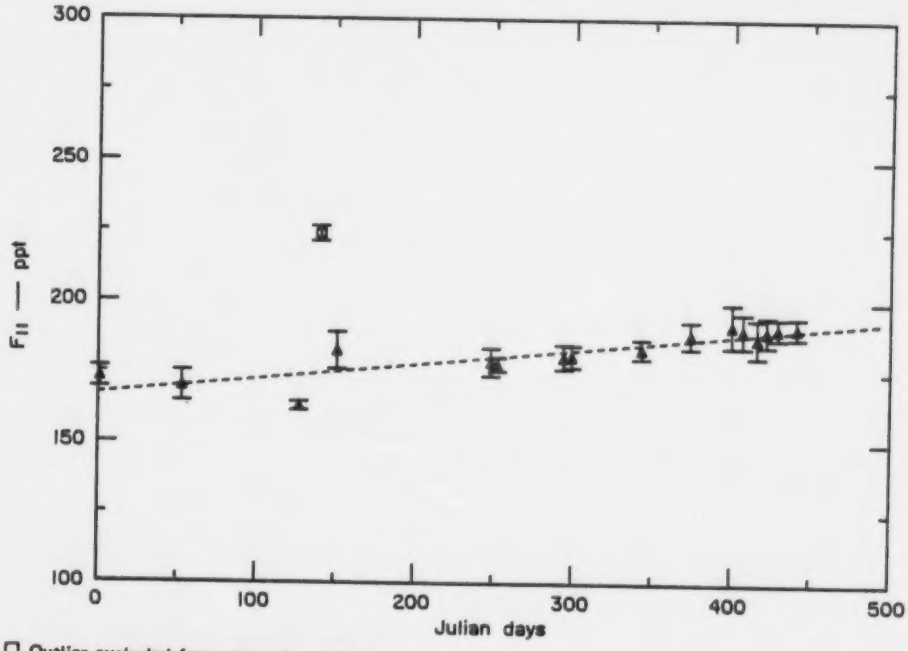
Unlike N_2O, fluorocarbon 12 (CCl_2F_2,F12) and fluorocarbon 11 (CCl_3F,F11) both appear to be increasing steadily. In December 1978 the CCl_2F_2 and CCl_3F levels in the northern hemisphere troposphere had mean values of 250 ppt and 150 ppt, respectively (Singh et al., 1979a). Tables 4 and 5 show that in early 1981 these concentrations were closer to 300 ppt and 190 ppt, respectively. Thus a perceptible change in the atmospheric levels of these man-made fluorocarbons continues to take place. Figures 4 and 5 show the trend in the tropospheric levels of F12 and F11 during the period of this study (December 1979 through February 1981). The regression analysis* indicates an average growth rate of 25 ppt per year for F12 and 19 ppt per year for F11. Using

*The points shown as squares are outliers and are excluded from the regression analysis.



□ Outlier excluded from regression analysis

FIGURE 4 FLUOROCARBON 12 CONCENTRATION VERSUS DAYS



□ Outlier excluded from regression analysis

FIGURE 5 FLUOROCARBON 11 CONCENTRATION VERSUS DAYS

December 1979 as the base period, atmospheric growth rates of about 9 percent per year and 11 percent per year for F12 and F11, respectively, are calculated. These rates are only slightly lower than those determined during the 1975-1978 period (Singh et al., 1979a; 1979b). Thus our data suggests that despite extensive efforts, there has been only a marginal reduction in the emissions of fluorocarbons on a global basis.

Figures 6 and 7 show the relatively low background concentrations of fluorocarbon 113 (CCl_2FCClF_2,F113) and fluorocarbon 114 ($CClF_2CClF_2$,F114). Although no trends are clear, the background concentrations of these species are about 25 ppt and 15 ppt, respectively. It is clear from Figures 6 and 7 that a small trend would be lost in the noise level. The background levels of F113 and F114 in early 1978 were determined to be about 19 ppt and 12 ppt, respectively (Singh et al., 1979a, 1979b). Thus it appears that the rate of growth of F113 and F114 over the last three years has been less than 10 percent per year.

HALOMETHANES

Methyl chloride (CH_3Cl), methyl bromide (CH_3Br), and methyl iodide (CH_3I) are the only three known halocarbons with predominant natural sources. The most abundant natural halocarbon is methyl chloride. Figure 8 shows the lack of trend in its atmospheric abundance and an average concentration of about 750 ppt. This average concentration is very similar to levels we have reported from other locations. Except for one data point, the trend for methyl bromide is similar, with an average concentration of 10 to 12 ppt (Figure 9). Because of their very low background concentrations (Tables 4 and 5), both methyl bromide and methyl iodide show considerable variability. It is interesting to note that higher methyl bromide levels seem to coexist with lower methyl iodide levels and vice versa (Figures 9 and 10). Average methyl iodide concentrations of 2 to 5 ppt near a marine site are comparable to what we have reported earlier. Unlike methyl chloride and methyl bromide, we are unable to see any elevation of methyl iodide levels in urban areas (Singh et al., 1980), suggesting an exclusive natural (oceanic) source.

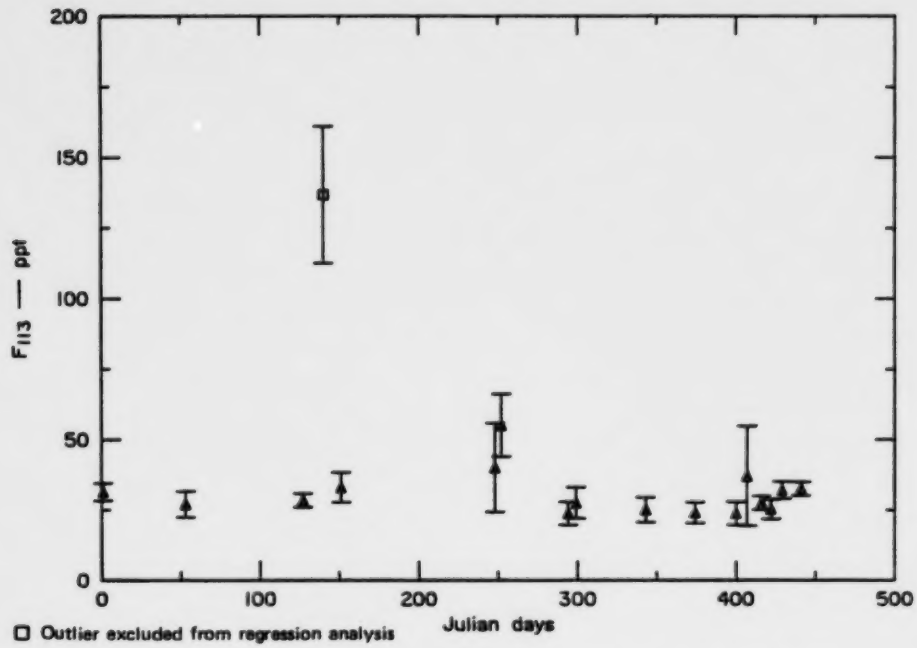


FIGURE 6 FLUOROCARBON 113 CONCENTRATION VERSUS DAYS

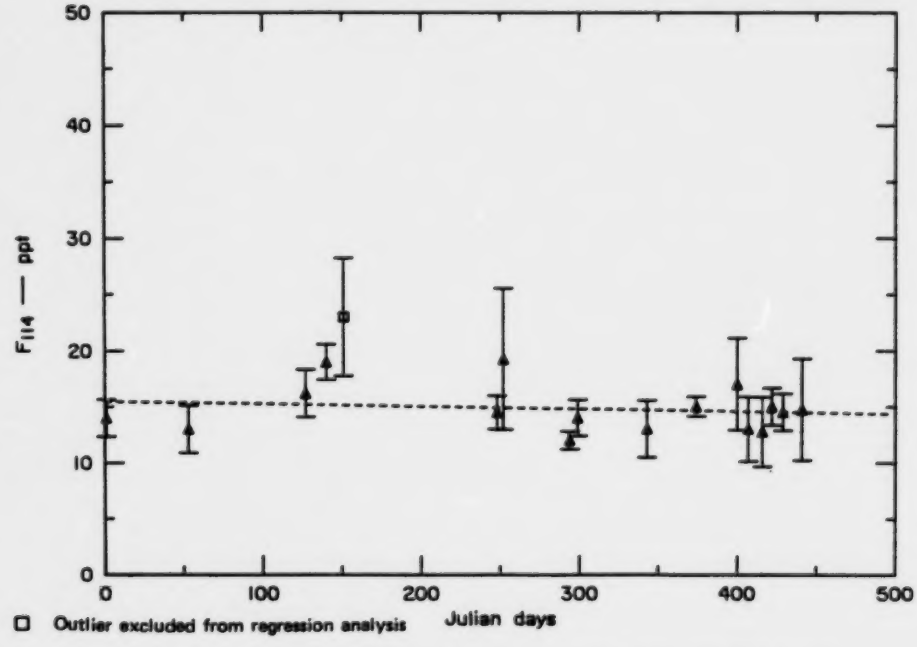


FIGURE 7 FLUOROCARBON 114 CONCENTRATION VERSUS DAYS

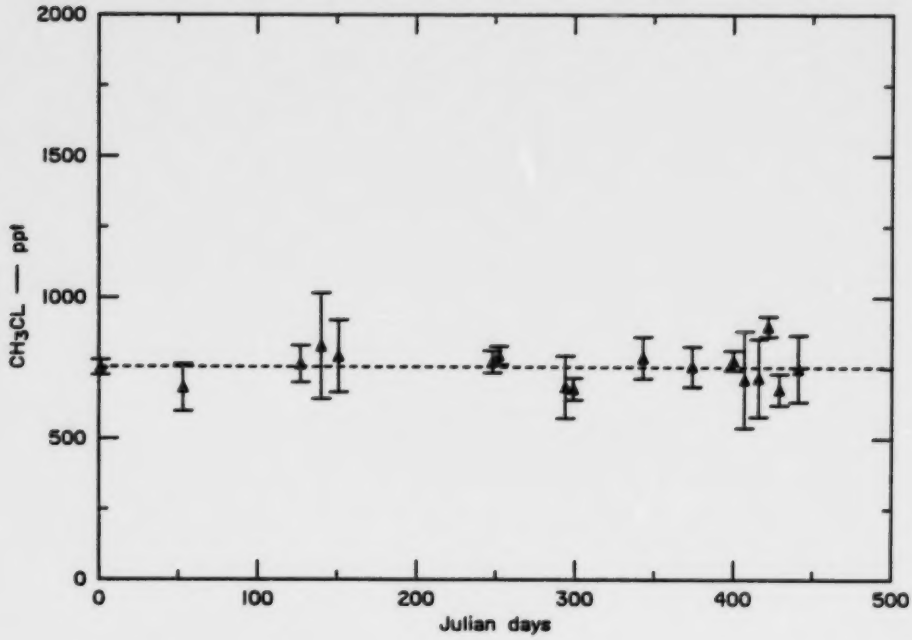


FIGURE 8 METHYL CHLORIDE CONCENTRATION VERSUS DAYS

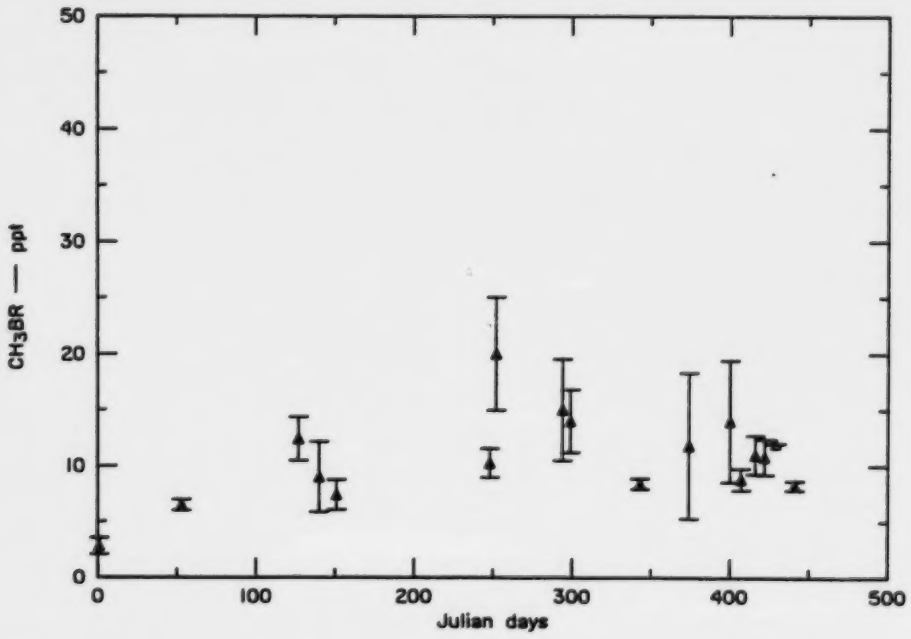


FIGURE 9 METHYL BROMIDE CONCENTRATION VERSUS DAYS

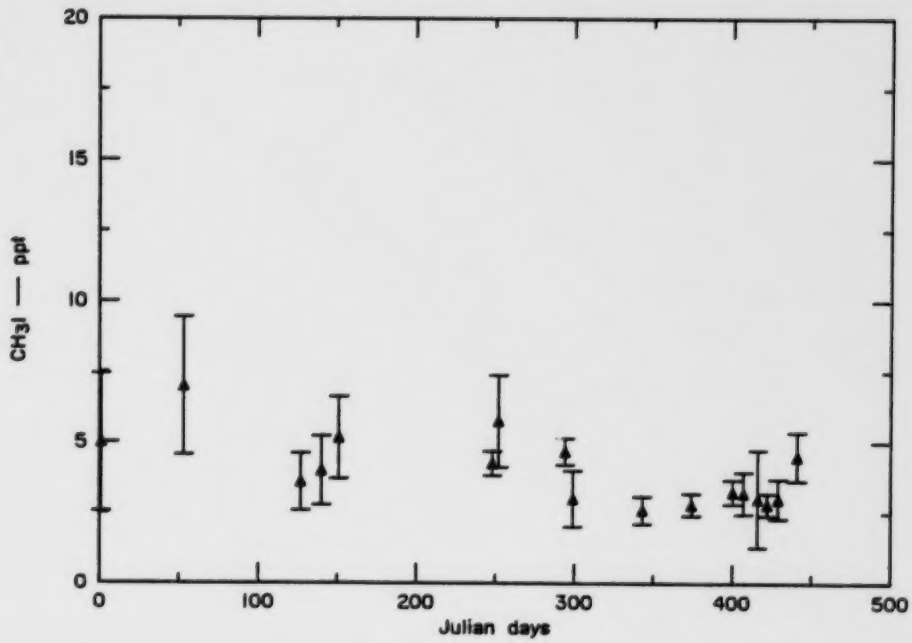


FIGURE 10 METHYL IODIDE CONCENTRATION VERSUS DAYS

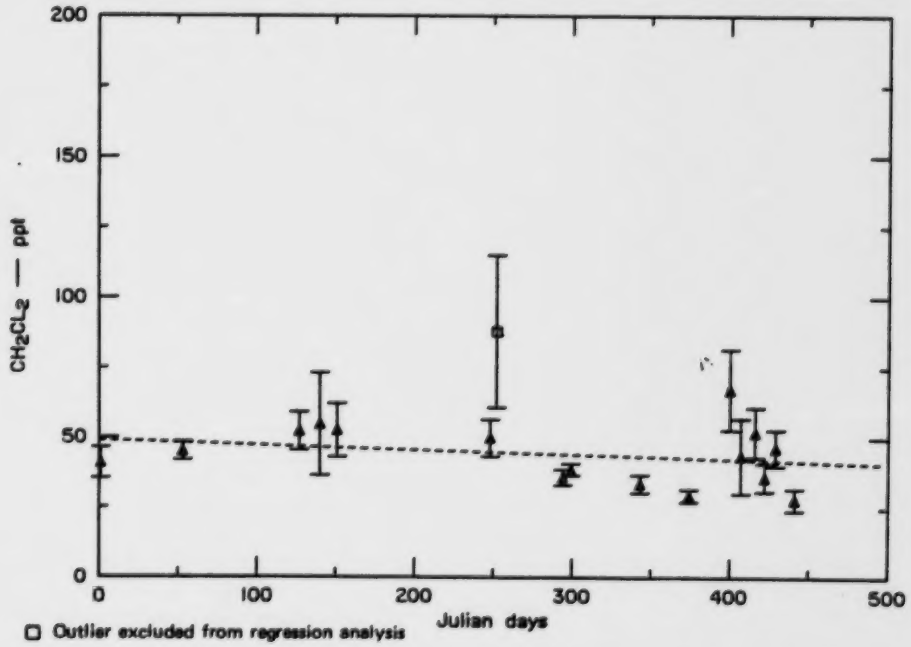


FIGURE 11 METHYLENE CHLORIDE CONCENTRATION VERSUS DAYS

Monohalomethanes are the only halocarbons with known and significant natural sources. No evidence exists to support natural sources for the other halomethanes, such as methylene chloride (CH_2Cl_2), chloroform ($CHCl_3$), and carbon tetrachloride (CCl_4), measured in this study. It is clear from Tables 4 and 5 and Figure 11 that methylene chloride has a background concentration of 50 ppt, but no clear trend is visible. The apparent declining trend in methylene chloride concentration may reflect seasonal variations in emission patterns--chloroform (Figure 12) also shows a significant scatter with an average background concentration of 20 ppt. Part of the scatter in chloroform concentrations may be attributable to the earlier reported chloroform contamination of coastal waters (Singh et al., 1977).

Unlike methylene chloride and chloroform, carbon tetrachloride shows little variability (Figure 13). Its high background concentration (135 ppt), dispersed and minor existing sources, and a long atmospheric lifetime (Singh et al., 1979b) all contribute to its low atmospheric variability. Although the carbon tetrachloride levels are clearly increasing in the troposphere, this increase is relatively small. Our regression analysis shows an average increase of about 5 ppt per year (~4 percent per year).

HALOETHANES

Four haloethanes were measured. These were ethyl chloride (C_2H_5Cl), 1,2 dichloroethane (CH_2ClCH_2Cl), 1,2 dibromoethane (CH_2BrCH_2Br) and 1,1,1 trichloroethane (CH_3CCl_3). To the best of our knowledge, no previous measurements of background levels of ethyl chloride and 1,2 dichloroethane have been reported. Measured background levels of about 10 to 20 ppt for ethyl chloride (Figure 14) and 40 to 50 ppt for 1,2 dichloroethane (Figure 15) are consistent with available emissions data. These levels are significantly lower than the measured urban levels for both of these species (Singh et al., 1980). Typical average concentrations of 1,2 dibromoethane are an order of magnitude lower than those of 1,2 dichloroethane and vary between 2 to 10 ppt (Figure 16). 1,1,1 trichloroethane is a most important haloethane with a high and rapidly increasing background burden. Figure 17 shows the atmospheric growth of 1,1,1 trichloroethane during the period of this study. With the help of regression

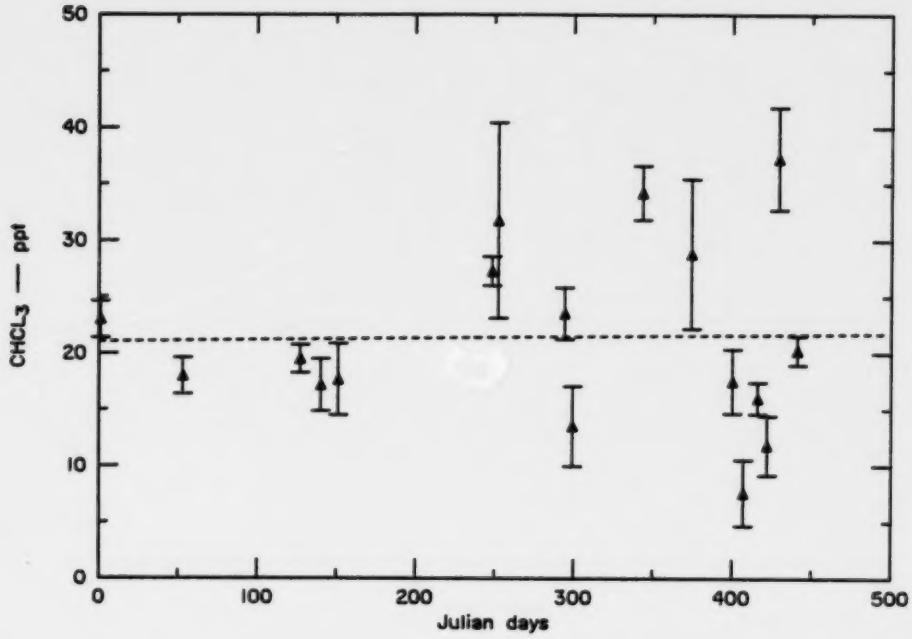


FIGURE 12 CHLOROFORM CONCENTRATION VERSUS DAYS

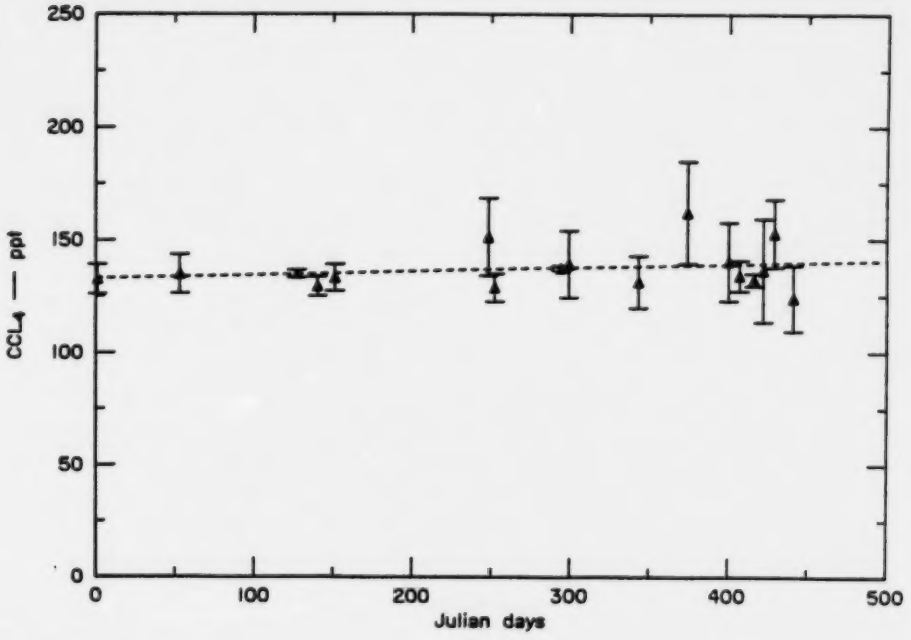


FIGURE 13 CARBON TETRACHLORIDE CONCENTRATION VERSUS DAYS

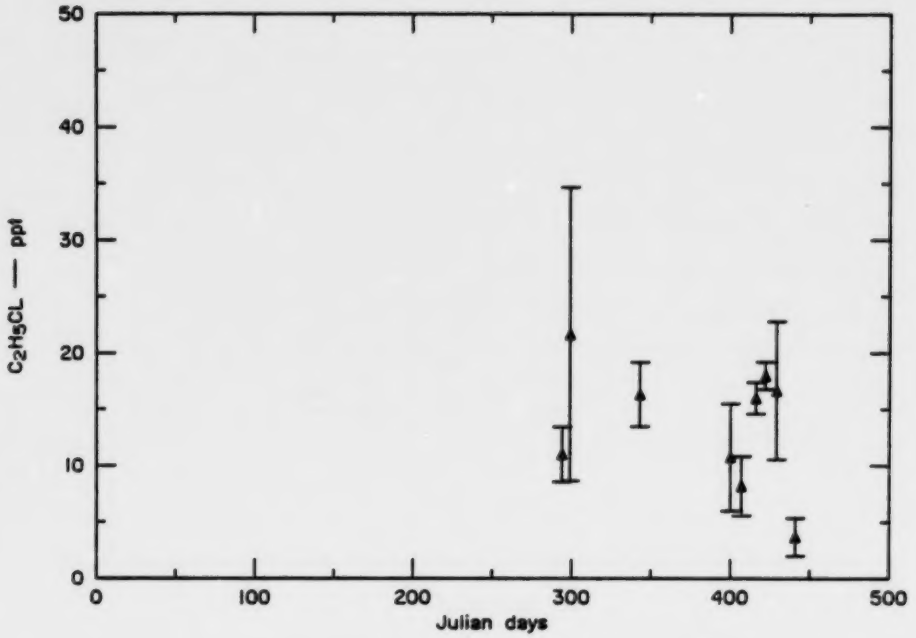


FIGURE 14 ETHYL CHLORIDE CONCENTRATION VERSUS DAYS

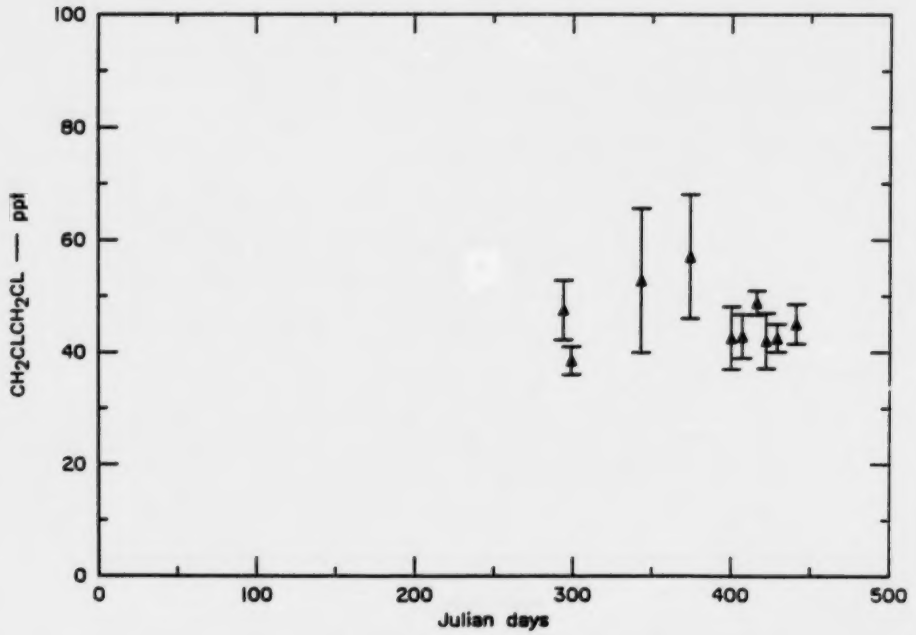


FIGURE 15 1,2 DICHLOROETHANE CONCENTRATION VERSUS DAYS

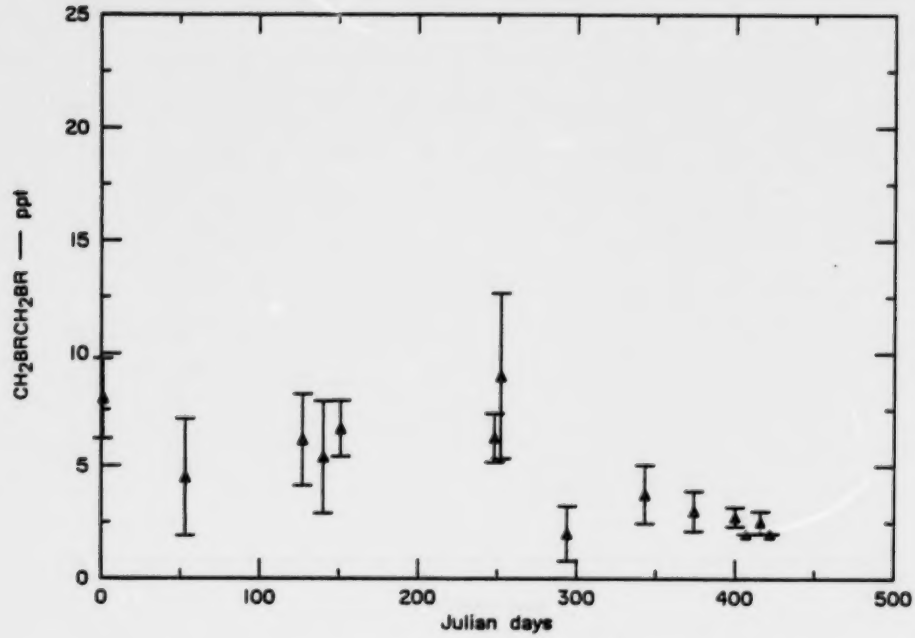


FIGURE 16 1,2 DIBROMOETHANE CONCENTRATION VERSUS DAYS

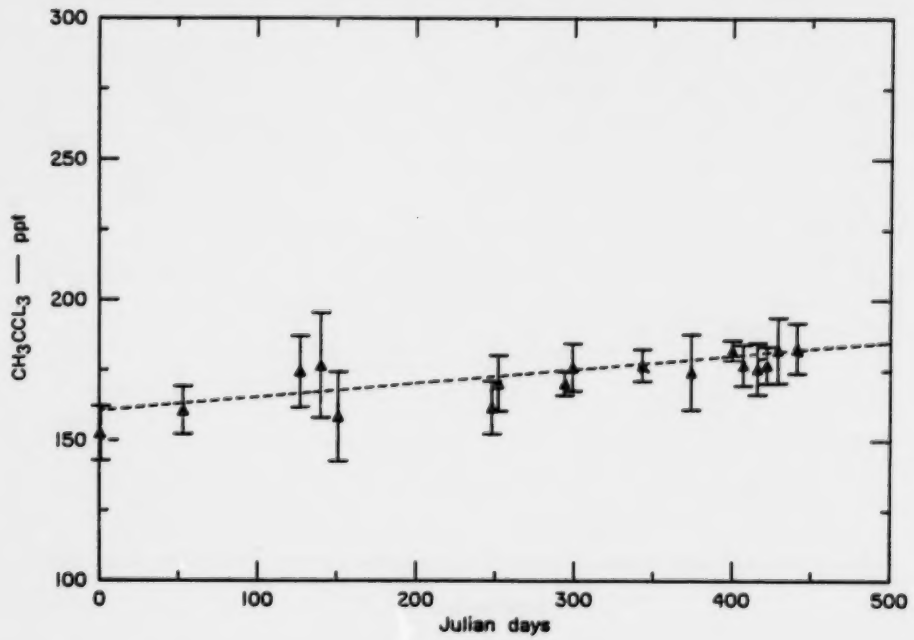


FIGURE 17 1,1,1 TRICHLOROETHANE CONCENTRATION VERSUS DAYS

analysis we compute a growth rate of 18 ppt per year. With a base value of 160 ppt in December 1979, an average annual 11 percent growth rate is calculated. The present midlatitude levels of about 180 ppt in the northern hemisphere can be compared with levels of about 130 ppt in early 1978 at this latitude (Singh et al., 1979a, 1979b).

CHLOROETHYLENES

Both trichloroethylene (C_2HCl_3) and tetrachloroethylene (C_2Cl_4) were measured. The background concentration of trichloroethylene (10 to 20 ppt) is consistent with previous measurements (Singh et al., 1979a), but no clear trends are discernible. On the average, a slight reduction in trichloroethylene levels appears to be occurring (Figure 18). The background concentration levels of tetrachloroethylene (Tables 4 and 5) are two to three times those of trichloroethylene. An average background concentration of about 50 ppt observed in this study is slightly higher than the 40 to 45 ppt levels reported earlier for this latitude (Singh et al., 1979a; 1979b). During the period of this study a small declining trend in tetrachloroethylene levels was observable (Figure 19).

NONMETHANE HYDROCARBONS

Six nonmethane hydrocarbons were measured. These were acetylene (C_2H_2), ethylene (C_2H_4), ethane (C_2H_6), propane (C_3H_8), n-butane ($n\text{-}C_4H_{10}$) and i-butane ($i\text{-}C_4H_{10}$). A considerable scatter in acetylene levels was observed (Tables 4 and 5). The lowest measured concentrations of about 0.2 ppb are considered representative of the free troposphere. These are in good agreement with background tropospheric levels reported by Cronn and Robinson (1979). The fluctuations in the levels of ethylene are so substantial (Tables 4 and 5) that no information regarding its geochemical background can be inferred. It is logical to assume that unknown but substantial local sources of ethylene exist in the Point Arena area.

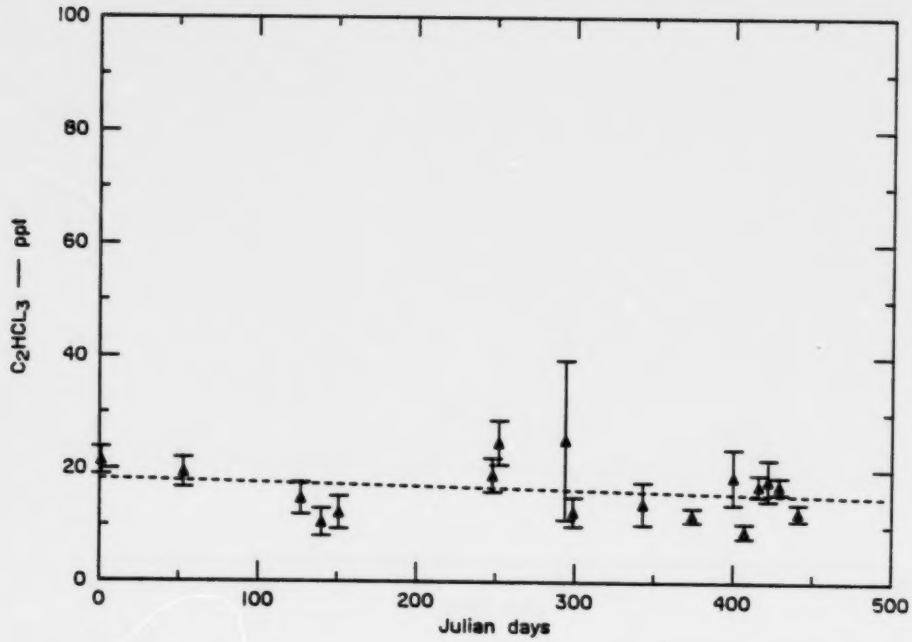


FIGURE 18 TRICHLOROETHYLENE CONCENTRATION VERSUS DAYS

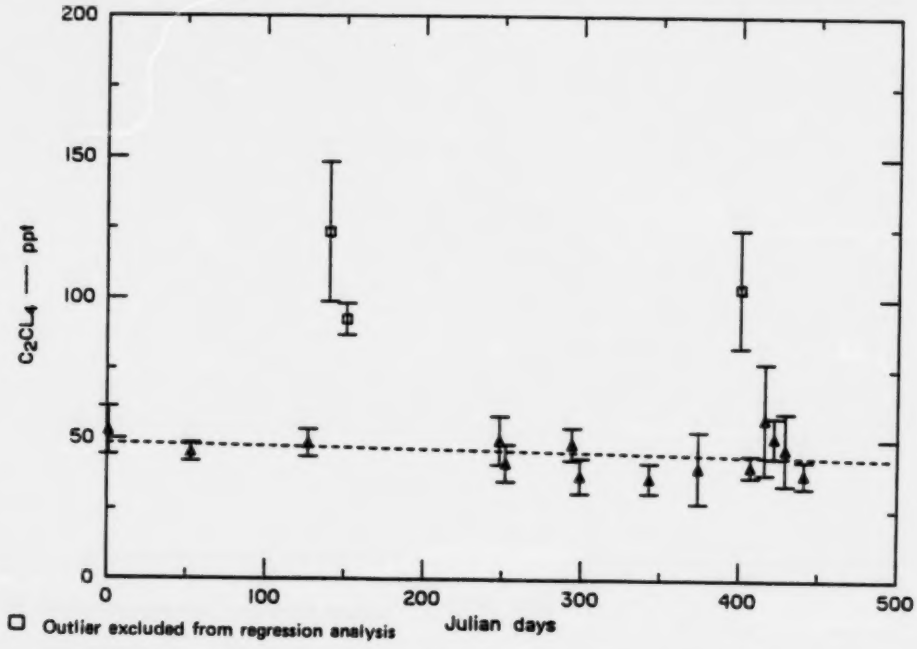


FIGURE 19 TETRACHLOROETHYLENE CONCENTRATION VERSUS DAYS

A substantial global background of ethane has already been reported (Singh et al., 1979a; 1979b). If we exclude those measurements in which a clear contamination is evident, a background of about 1.5 to 2 ppb is found (Figure 20). This is about four to five times the measured background of about 0.4 ppb for propane (Tables 4 and 5). These measurements can be compared with the recent upper-tropospheric and stratospheric measurements of Rudolph et al. (1980), who report tropospheric background levels of 1.5 ppb ethane and 0.3 ppb propane. Although substantial natural sources of ethane and propane are known to exist, no global emissions inventories are available.

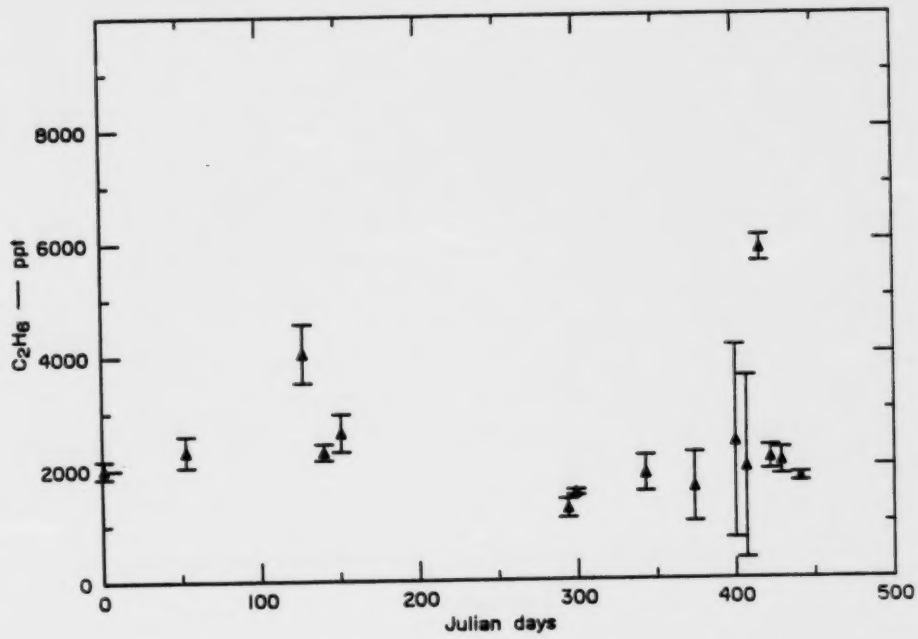


FIGURE 20 ETHANE CONCENTRATION VERSUS DAYS

SECTION 5

FORMATION OF SECONDARY PRODUCTS FROM GLOBALLY DISTRIBUTED TRACE CHEMICALS

A part of this study is devoted to the understanding of the secondary products that must be produced from the primary species being measured. As a first step in this direction we considered the oxidation of nonmethane hydrocarbons in the troposphere and the stratosphere. If we consider only the very clean atmosphere (above 3 km), ethane and propane appear to be the dominant hydrocarbons (Singh et al., 1979a; 1979B; Rudolph et al. 1980). Therefore we studied the secondary products of these hydrocarbons and found that their products are potentially important carriers of reactive nitrogen in the troposphere and the stratosphere. The distribution of the intermediate oxygenates and organic nitrogen compounds between 2 and 20 km is described in the following section.

ANALYSIS

Table 6 summarizes the atmospheric conditions that apply to the midlatitude region in the northern hemisphere. For the purposes of this analysis, three levels representative of the lower troposphere (~2 km), upper troposphere (~9 km), and the lower stratosphere (~15 km) are chosen. Based on available measurements, ethane (C_2H_6) and propane (C_3H_8) are found to be the dominant nonmethane hydrocarbons. In the lowest troposphere, other hydrocarbons (e.g., butanes, ethylene, isoprene) may also be important (Rudolph et al., 1979). However, their ubiquitousness in other parts of the troposphere has not yet been fully established. Although we limit the analysis of this study to ethane and propane, the presence of other hydrocarbons would further strengthen the conclusions of this study.

Table 6

ATMOSPHERIC ABUDANCE OF TRACE SPECIES OF INTEREST AT SELECTED ELEVATIONS

Atmospheric Region	Temperature (K)	Trace Species Concentrations (ppb)						Free Radical Concentrations molec/cm^3	
		CH_4	C_2H_6	C_3H_8	HCHO	NO_x	Average NO_2/NO ratio (daytime)	OH	Cl
Lower troposphere (~ 2 km)	285	1600	1.5	0.25	0.4	0.015	2.0	10^6	(~ 0)
Upper troposphere (~ 9 km)	240	1600	1.5	0.20	0.04	0.15	0.5	5×10^5	(~ 0)
Lower stratosphere (~ 15 km)	215	1400	0.3	0.01	0.035	0.6	0.5	5×10^5	5×10^3

Methane data in Table 6 are taken from Hudson and Reed (1979). Ethane and propane concentrations are from Rudolph et al. (1980). Formaldehyde data are available from one-dimensional models and have been verified by a limited number of measurements (Ehhalt and Tönnissen, 1980). NO_x data are based on the recent work of Kley et al. (1981) and for the stratosphere are taken from Hudson and Reed (1979). Daytime average NO_2/NO ratios are derived from the global photochemical model of Liu (1981). OH levels chosen here (daily average) are consistent with the best estimates of OH from models: Direct OH measurements suggest higher OH levels than those used in Table 6. Levels higher than those listed in Table 6 make the results of this study correspondingly more important. Chlorine atom concentrations have not been measured below 30 km. The Cl atom concentration listed in Table 6 is derived from a one-dimensional model (Rudolph et al., 1980). Rate constant symbols and data utilized in this study are presented in Table 7.

Oxidation of ethane is initiated when an OH or Cl radical abstracts hydrogen. The C_2H_5 radical is converted to a peroxide radical and then to acetaldehyde (CH_3CHO). These steps are similar to those in the oxidation of CH_4 to formaldehyde. The propane oxidation also proceeds along the same lines but the OH attack occurs at the middle carbon leading to the formation of acetone (CH_3COCH_3).

$$CH_4 \xrightarrow[Cl]{OH} CH_3 \xrightarrow{O_2} CH_3O_2 \xrightarrow{NO} CH_3O \xrightarrow{O_2} HCHO \xrightarrow[OH,Cl]{h\nu} \text{products} \qquad (1)$$

$$C_2H_6 \xrightarrow[Cl]{OH} C_2H_5 \xrightarrow{O_2} C_2H_5O_2 \xrightarrow{NO} C_2H_5O \xrightarrow{O_2}$$

$$CH_3CHO \xrightarrow[OH,Cl]{h\nu} \text{products} \qquad (2)$$

Table 7

LIST OF RATE CONSTANTS USED IN THIS STUDY

Reaction	Rate Constants*	Source†
$CH_4 + OH \rightarrow$	$k_1 = 2.4 \times 10^{-12} \exp(-1710/T)$	Hudson and Reed (1979)
$CH_4 + Cl \rightarrow$	$k_1' = 9.9 \times 10^{-12} \exp(-1359/T)$	Hudson and Reed (1979)
$C_2H_6 + OH \rightarrow$	$k_2 = 1.86 \times 10^{-11} \exp(-1230/T)$	Greiner (1970)
$C_2H_6 + Cl \rightarrow$	$k_2' = 7.3 \times 10^{-11} \exp(-61/T)$	Manning and Kurylo (1977)
$C_3H_8 + OH \rightarrow$	$k_3 = 1.82 \times 10^{-11} \exp(-675/T)$	Greiner (1970) and Darnall et al. (1978)
$C_3H_8 + Cl \rightarrow$	$k_3' = 1.36 \times 10^{-10} \exp(+44/T)$	Lewis et al. (1980)
$HCHO + OH \rightarrow$	$k_7 = 1.1 \times 10^{-11}$	Stief et al. (1980)
$HCHO + Cl \rightarrow$	$k_7' = 9.2 \times 10^{-11} \exp(-68/T)$	Hudson and Reed (1979)
$HCHO \xrightarrow{h\nu}$	$k_7'' = 2.8 \times 10^{-5}$ ‡	Hendry et al. (1980)
$CH_3CHO + OH \rightarrow$	$k_8 = 1.5 \times 10^{-11}$	Atkinson et al. (1979)
$CH_3CHO + Cl \rightarrow$	$k_8' = 1.1 \times 10^{-10}$	Estimated from HCHO data
$CH_3CHO \xrightarrow{h\nu}$	$k_8'' = 1.4 \times 10^{-5}$ ‡	Hendry et al. (1980)
$CH_3COCH_3 + OH \rightarrow$	$k_9 = k_2$	Cox et al. (1980), Atkinson (1981)
$CH_3COCH_3 + Cl \rightarrow$	$k_9' = k_2'$	Atkinson (1981)
$CH_3COCH_3 \xrightarrow{h\nu}$	$k_9'' = 5 \times 10^{-6}$ ‡	Estimated from Calvert and Pitts (1966)
$CH_3C(O)O_2 + NO_2 \rightarrow$	$k_{10} = 1.4 \times 10^{-12}$	Cox and Roffe (1977)
$PAN \xrightarrow{\text{Thermal}}$	$k_{11} = 7.9 \times 10^{14} \exp(-12540/T)$ ‡	Cox and Roffe (1977)
$CH_3C(O)O_2 + NO \rightarrow$	$k_{12} = 2.4 \times 10^{-12}$	Cox and Roffe (1977)
$PAN + OH \rightarrow$	$k_{13} \leq 1.7 \times 10^{-13}$ at 300K§	Winer et al. (1977)
$PAN + Cl \rightarrow$	$k_{13}' = 2.8 \times 10^{-13}$ at 215K	Atkinson (1981)
$PAN \xrightarrow{h\nu}$	$k_{13}'' = 2 \times 10^{-8}$ (max) ‡	U.V. spectrum from Stephens (1969)

*All rate constants in units of cm^3 $molec^{-1}$ sec^{-1} unless otherwise indicated.

†Many of these references are compilations that also contain original sources of rate data.

‡In units of sec^{-1}.

§PAN + Cl rate constant is estimated by Atkinson (1981) to be half of C_2H_6 + Cl. Temperature dependence of PAN + OH and PAN + Cl reaction is estimated from C_2H_6 data.

$$CH_3CH_2CH_3 \xrightarrow[Cl]{OH} CH_3CHCH_3 \xrightarrow{O_2} CH_3CH(O_2)CH_3 \xrightarrow{NO}$$

$$CH_3CH(O)CH_3 \xrightarrow{O_2} CH_3COCH_3 \xrightarrow[OH,Cl]{h\nu} \text{products} \quad . \tag{3}$$

Overall we can summarize these sequences as follows:

$$CH_4 \xrightarrow{k_1, k_1'} HCHO \xrightarrow{k_7, k_7', k_7''} \text{products} \tag{4}$$

$$C_2H_6 \xrightarrow{k_2, k_2'} CH_3CHO \xrightarrow{k_8, k_8', k_8''} \text{products} \tag{5}$$

$$C_3H_8 \xrightarrow{k_3, k_3'} CH_3COCH_3 \xrightarrow{k_9, k_9', k_9''} \text{products} \quad . \tag{6}$$

Reactions (4), (5), and (6) are so similar that CH_3CHO and CH_3COCH_3 levels can be estimated by knowing the rate constants in these reaction sequences, as shown in Table 7, and the abundance of HCHO that has been relatively well characterized from 1-D models and limited measurements (Table 6). As a first approximation, the concentration of CH_3CHO from ethane and CH_3COCH_3 from propane can be estimated as follows:

$$[CH_3CHO]_{C_2H_6} = \left(\frac{k_2(C_2H_6)(OH) + k_2'(C_2H_6)(Cl)}{k_1(CH_4)(OH) + k_1'(CH_4)(Cl)}\right)\left(\frac{[HCHO]}{P1}\right) \tag{7}$$

$$[CH_3COCH_3]_{C_3H_8} = \left(\frac{k_3(C_3H_8)(OH) + k_3'(C_3H_8)(Cl)}{k_1(CH_4)(OH) + k_1'(CH_4)(Cl)}\right) \times$$

$$\left(\frac{[HCHO]}{P2}\right)(0.8) \tag{8}$$

where

$$p_1 = \frac{k_8(OH) + k_8'(Cl) + k_8''}{k_7(OH) + k_7'(Cl) + k_7''} \tag{9}$$

$$p_2 = \frac{k_9(OH) + k_9'(Cl) + k_9''}{k_7(OH) + k_7'(Cl) + k_7''} \quad . \tag{10}$$

The quantities in p_1 and p_2 essentially account for the fact that the CH_3CHO and CH_3COCH_3 decay rates are slower than HCHO. It is noted here that a small part of OH attack in propane can occur at the end carbon, leading largely to the formation of propionaldehyde. We have chosen to multiply the estimated CH_3COCH_3 concentration (Eq. 8) by 0.8 to correct for this minor branching as suggested by Hanst (1981).

The intermediates acetaldehyde and acetone are the precursors of PAN. Once CH_3CHO is formed it is either photolyzed or can react with OH or Cl radicals. The photolysis reaction results in a CH_3O_2 radical formation that can eventually form HCHO. In the case of acetaldehyde, the reaction with OH is of most interest. Photolysis is the key reaction for acetone, reaction with OH being too slow. The following sequence is known to take place (Cox and Roffey, 1977; Hendry and Kenley, 1977):

$$CH_3CHO + OH \xrightarrow[2O_2]{k_8} CH_3C(O)O_2 + H_2O \tag{11}$$

$$CH_3COCH_3 + \xrightarrow[2O_2]{k_9''(h\nu)} CH_3C(O)O_2 + CH_3O_2 \tag{12}$$

$$CH_3C(O)O_2 + NO_2 \underset{k_{11}}{\overset{k_{10}}{\rightleftharpoons}} CH_3C(O)O_2NO_2 \text{ (PAN)} \tag{13}$$

$$CH_3C(O)O_2 + NO \xrightarrow{k_{12}} CH_3 + CO_2 + NO_2 \qquad (14)$$

$$PAN + OH \xrightarrow{k_{13}} \text{products} \qquad (15)$$

$$PAN + Cl \xrightarrow{k_{13}'} \text{products} \qquad (16)$$

$$PAN \xrightarrow{k_{13}''(h\nu)} \text{products} \quad . \qquad (17)$$

Assuming a steady state for PAN, the following concentration expression can be derived:

$$PAN = \left(\frac{k_{10}}{k_{11}k_{12}}\right) \times$$

$$\left[\frac{k_8(CH_3CHO)(OH) + k_9''(CH_3COCH_3)}{1 + \left(\frac{1}{k_{11}} + \frac{k_{10}(NO_2)}{k_{11}k_{12}(NO)}\right)\left(k_{13}(OH) + k_{13}'(Cl) + k_{13}''\right)}\right]\left(\frac{NO_2}{NO}\right) \quad . \qquad (18)$$

A number of observations regarding (11)-(17) must be made. First, the reactions $CH_3CHO + Cl$, $CH_3COCH_3 + OH$, and $CH_3COCH_3 + Cl$, even if they were to form $CH_3C(O)O_2$ radicals, are slow and can be neglected (Table 7). Similarly, $CH_3C(O)O_2 + HO_2$ is unimportant. The steep temperature dependence of k_{11} plays a dominant role in the atmospheric distribution of PAN. Temperature-dependent rate constants for k_{10} and k_{12} are not available. However, the ratio k_{10}/k_{12} [eq. (18)] is expected to be relatively temperature-independent.

The series of reactions (11) through (17) have no analogues in the oxidation of HCHO. The compound peroxy formyl nitrate has never been observed. Formyl radicals do not react with oxygen to form peroxyacyl radicals.

Instead, the hydrogen is removed, yielding CO and HO_2 radicals (Hanst and Gay, 1977). Eq. (18) was independently verified at 300K for the conditions operating within a smog chamber (Singh et al., 1979c).

Expression (18) is derived assuming a stationary atmosphere. For the upper troposphere, exchange with the lower troposphere could provide an important removal mechanism because of the rapid decomposition of PAN in the lower troposphere. Thus the upper-tropospheric calculations have been performed with—as well as without—this sink. A 60-day exchange rate ($k_e = 1.9 \times 10^{-7}$ sec^{-1}) with the lower troposphere is utilized:

$$\text{PAN (upper troposphere)} \xrightarrow{k_e} \text{Loss (lower troposphere)} \quad . \tag{19}$$

RESULTS AND DISCUSSION

From the data provided in Tables 6 and 7, equations (7), (8), and (18) can be readily solved to obtain an estimate of the expected concentrations of CH_3CHO, CH_3COCH_3, and PAN. These results for the three important regions of the atmosphere are summarized in Table 8. It is clear that ethane alone can produce about 20 ppt of acetaldehyde in the lower troposphere. In a manner similar to HCHO, a rapid drop with altitude is observed in the troposphere. The increase in CH_3CHO in the lower stratosphere is attributable to the important role of Cl atoms in the oxidation of ethane. The trend for CH_3COCH_3 is very similar. Its much higher concentration at the lower troposphere is largely attributable to its much slower loss rate.

The distribution of PAN in the atmosphere is found to be dramatically different from that of the intermediate products acetaldehyde and acetone. PAN levels of 17 ppt, 360 ppt, and 85 ppt are estimated for the lower troposphere, upper troposphere, and the lower stratosphere, respectively. When the exchange process described in reaction (19) is considered, PAN concentrations in the upper troposphere decrease to about 90 ppt. The PAN distribution (Table 8) is largely a result of the highly temperature-dependent sinks of PAN. In the lower troposphere, the thermal decomposition of PAN (reaction k_{11}) is extremely rapid and is the only important sink. This thermal loss of

Table 8

ESTIMATED CONCENTRATION OF ACETALDEHYDE, ACETONE, AND PAN

Atmospheric Region	CH_3CHO (ppt) (from C_2H_6)	CH_3COCH_3 (ppt) (from C_3H_8)	PAN (ppt)*
Lower troposphere	22	111	17†
Upper troposphere	3	15	90∓-360†
Lower stratosphere	7	3	85†

*Parts per trillion.

†Assumes stationary atmosphere.

∓Assuming a 60-day exchange between the upper tropospheric and lower tropospheric air.

PAN becomes relatively unimportant at the colder temperatures of the upper troposphere and the lower stratosphere. The UV absorption cross section of PAN is not highly reliable (Stephens, 1969) but photolytic loss of PAN below the ozone layer is relatively small (k_{13}'). PAN + OH and PAN + Cl reactions provide the important chemical removal processes at these higher altitudes. For the upper troposphere, exchange with the lower troposphere is an important removal process.

Estimated levels of PAN shown in Table 8 clearly point to the potential importance of organic nitrogen compounds in the atmosphere. Comparison of NO_x data from Table 6 with PAN levels shows that in the troposphere NO_x contained in its organic form may be as much or more abundant as the inorganic form. In the middle troposphere the reactive organic nitrogen could be 50 to 100 percent of the inorganic reactive nitrogen ($NO_x + HNO_3$). In the lower stratosphere only 10 to 15 percent of all nitrogen oxides may exist in their organic form. At 20 km, PAN levels are estimated to be a quarter of 15-km levels.

The calculations in this study have been made for those conditions listed in Table 6. The suggested higher OH levels and the presence of other

hydrocarbons (Rudolph et al., 1979) could easily double the estimated CH_3CHO, CH_3COCH_3, and PAN concentrations in the lower troposphere. In addition, transport from polluted areas may also provide an additional source (Hendry and Kenley, 1977; Crutzen, 1979). Chlorine atom levels in the lower troposphere could be a factor of 2 to 4 lower than those utilized in Table 6 (Rudolph et al., 1980). This could reduce estimated PAN levels in the lower stratosphere by a factor of about 2 (~40 ppt). The effect is not linear because Cl atoms are both an important source as well as a sink for PAN. Part of this reduction could also be compensated by a higher than 0.5 NO_2/NO ratio in the lower stratosphere. Similarly, k_{12} may be larger than utilized in Table 7 (Sander and Watson, 1980). This will tend to reduce PAN levels in the lower troposphere but will have virtually no effect elsewhere. The pressure dependence of $RO_2 + NO_2 + M$ (forward reaction 13) has been measured to be negligible (Cox and Tyndall, 1979; Adachi and Basco, 1980). Sander and Watson (1980), however, do find a pressure dependence. If true, its effect would be to reduce estimated PAN levels with increasing altitude. The significance of the conclusions of this study, however, remains unaltered despite these uncertainties in our current understanding of the atmosphere. A schematic of the vertical distribution of PAN, when these uncertainties are considered, is shown in Figure 21.

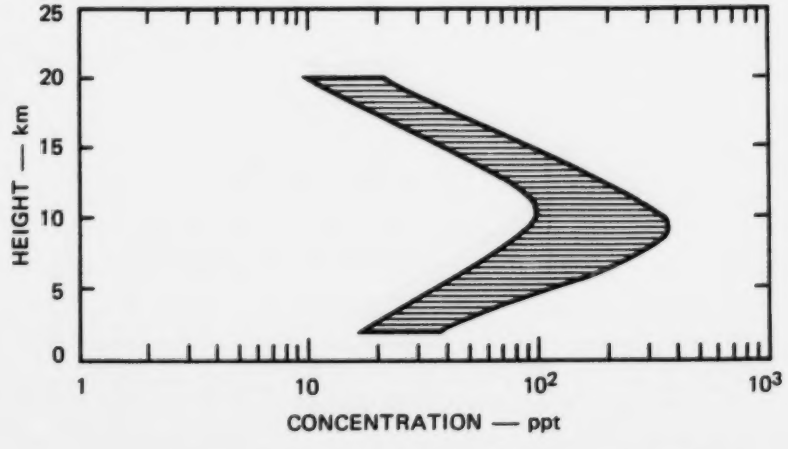


FIGURE 21 SCHEMATIC OF PAN PROFILE IN THE ATMOSPHERE

Since PAN and NO_2 equilibrium can shift rapidly with temperature [reaction (13)], PAN can regenerate NO_2 at warmer temperatures. Thus, a constant exchange of PAN and NO_2 in the lower and upper troposphere associated with turbulent weather conditions can exist. Rapid absorption of UV light above the ozone layer could cause PAN to transport inorganic nitrogen from the lower to the upper stratosphere. In the future, higher Cl concentration in the lower stratosphere (from man-made activities such as release of halocarbons) could increase this role of PAN. Similarly, increasing levels of man-made pollution (including those from aircraft exhaust) could increase the levels of these and other nonmethane hydrocarbons, thereby further increasing the organic content of reactive nitrogen.

Although measurements of acetaldehyde and acetone at these levels must await further developments in instrumentation, methods currently exist (electron capture gas chromatography) to measure PAN at these estimated concentration levels (Singh et al., 1979b). In addition, one should attempt to apply the spectroscopic method. When the solar spectrum is recorded at grazing incidence through the upper atmosphere, the strong PAN bands at 795 cm^{-1} and 1165 cm^{-1} should appear.

These preliminary calculations can be further improved by the exercise of more sophisticated photochemical models and the development of more accurate UV absorption (e.g., acetone, PAN) and temperature-dependent rate-constant (especially PAN + OH, PAN + Cl, and acetone + OH reactions) data. The possibility that methane-initiated reactions ($CH_3O_2 + NO_2 \rightarrow CH_3OONO_2$; $CH_3O + NO_2 \rightarrow CH_3ONO_2$) may provide additional sources of organic nitrogen compounds, especially at the colder temperatures of the upper troposphere and the stratosphere, should be further explored. Other peroxy nitrates may also contribute in small degree to this organic reservoir of NO_x. These include peroxy nitric acid, peroxy propionyl nitrate, peroxy benzoyl nitrate, and halogenated peroxy nitrates.

SECTION 6

SUMMARY OF RESULTS

Table 9 presents January 1981 average background concentrations of a large number of chemicals, based on measurements conducted at midlatitudes in the northern hemisphere. Data for carbon tetrafluoride and fluorocarbon 22 are taken from Penkett et al. (1980) and Rasmussen et al. (1980), respectively.

Table 10 shows the average atmospheric growth rate of selected chemicals in the troposphere. As shown in Table 10, the growth rates for N_2O is found to be immeasurably small ($\leq \pm 0.5$ percent per year). Fluorocarbon 12 and fluorocarbon 11 continue to increase at a rate of 25 ppt per year (~9 percent per year) and 19 ppt per year (~11 percent per year). Atmospheric growth rates of fluorocarbons 113 and 114 are less than 10 percent per year. The atmospheric burden of carbon tetrachloride is found to be increasing at a rate of about 5 ppt per year (~4 percent per year). The most rapidly increasing halocarbon is 1,1,1 trichloroethane. Its growth rate is measured to be 18 ppt per year (~11 percent per year). No mean trend is observable in the background levels of naturally occurring halocarbons such as methyl chloride, methyl bromide, and methyl iodide. Among the man-made chemicals, background levels of such compounds as methylene chloride and tetrachloroethlene, ethylene dichloride and trichloroethylene are relatively constant or may be declining slightly.

A consideration of budgets (Table 11) shows that there were about 3.7 ppb of chloride atoms in the northern hemisphere troposphere (mid-latitudes). Fully 80 percent of this chlorine is of man-made origin. When compared to the chlorine budget of 3.0 ppb for early 1978 (Singh et al., 1979a), it is evident that the chlorine burden in the troposphere has increased by about 25 percent

Table 9

AVERAGE BACKGROUND CONCENTRATIONS (January 1981)
OF IMPORTANT TRACE CHEMICALS
IN THE NORTHERN HEMISPHERE (40^{o}N)

Chemicals	Major Source	Average Background Concentration
Nitrous oxide	N	312 ppb
Carbon tetrafluoride	A	65 ppt
Sulfur hexafluoride	A	0.4 ppt
Fluorocarbon 12	A	300 ppt
Fluorocarbon 11	A	190 ppt
Fluorocarbon 22	A	50 ppt
Fluorocarbon 113	A	25 ppt
Fluorocarbon 114	A	15 ppt
Methyl chloride	N	750 ppt
Methyl bromide	N,A	12 ppt
Methyl iodide	N	3 ppt
Methylene chloride	A	50 ppt
Chloroform	A	22 ppt
Carbon tetrachloride	A	135 ppt
Ethyl chloride	A	10 ppt
1,2 Dichloroethane	A	40 ppt
1,2 Dibromoethane	A	2 to 5 ppt
1,1,1 Trichlorethane	A	180 ppt
Trichloroethylene	A	15 ppt
Tetrachloroethylene	A	50 ppt
Acetylene	A	0.2 ppb
Ethane	N	2.0 ppb
Propane	N	0.4 ppb

Table 10

AVERAGE ATMOSPHERIC GROWTH RATES OF SELECTED SPECIES FROM LATE 1979 TO EARLY 1981 IN THE NORTHERN HEMISPHERE ($40^{\circ}N$)

Compound	Average Growth Rate
N_2O	No change ($<\pm 2$ ppb per year)
CH_3Cl	No change ($<\pm 50$ ppt per year)
CCl_2F_2(F12)	25 ppt per year
CCl_3F(F11)	19 ppt per year
CCl_2FCClF_2(F113)	2 ppt per year
CCl_4	5 ppt per year
CH_3CCl_3	18 ppt per year

Table 11

TROPOSPHERIC CHLORINE, BROMINE, IODINE, AND FLUORINE ORGANIC BUDGETS FOR EARLY 1981 IN THE NORTHERN HEMISPHERE ($40^{\circ}N$)

Species	Budget (Northern Hemisphere) Midlatitude	Percentage Source Contribution	
		Man-made	Natural
Cl	3.7 ppb	80	20
Br	15 to 20 ppt	25 to 50	75 to 50
I	3 ppt	0	100
F	1.3 ppb	100	0

during the last three years. A similar increase in the fluorine budget (1.3 ppb versus 1.1 ppb) has also occurred. All of this fluorine is attributable to man-made sources. Of the 15 to 20 ppt of organic bromine, 25 to 50 percent is of man-made origin. Iodine, however, is all natural, with a budget of about 3 ppt or less. For short-lived species such as methyl iodide, surface measurements cannot be extended to the entire troposphere. The atmospheric burdens of organic bromine and iodine are both very low and possibly insufficiently characterized.

In addition, we find that minor atmospheric trace constituents can form secondary products that can play a more significant role than the parent molecule. An analysis of the fate of nonmethane hydrocarbons shows that they can oxidize to form significant amounts of organic nitrogen compounds in the unpolluted troposphere and the lower stratosphere. Our findings suggest that in the troposphere more than half of the reactive nitrogen exists in its combined organic form.

SECTION 7

FUTURE PLANS

The measurement program at Point Arena will continue as outlined in this report for the remainder of the second year. In the third year it is planned that measurements at Point Arena will be complemented by an interhemispheric profile of these species to extend the utility of the data and to relate them to global distributions and trends. These hemispheric profiles would for the first time establish the global distributions of a large number of chemicals for which no data is currently available (such as CH_2Cl_2, CH_2CClCH_2Cl, CH_3I, and CH_3Br). In addition, the north/south distributions of selected chemicals will be used to study their fate, and the chemistry of the natural atmosphere, as well as to provide a more rigorous interpretation of the Point Arena data.

REFERENCES

Adachi, H., and N. Basco, 1980: "The Reaction of CH_3O_2 Radicals with NO_2," Int. J. of Chem. Kinetics, Vol. 12, pp. 1-16.

Atkinson, R., K.R. Darnall, A.C. Lloyd, A.M. Winer, and J.N. Pitts, Jr., 1979: "Kinetics and Mechanisms of the Reaction of the Hydroxyl Radical with Organic Compounds in the Gas Phase," Adv. Photochem., 11, pp. 375-488.

Atkinson, R., 1981: Private communication, U.C. Riverside.

Calvert, J.G., and J.N. Pitts, Jr., 1966: Photochemistry (Wiley, New York).

Chameides, W.L., and R. Cicerone, 1978: "Effects of Nonmethane Hydrocarbons in the Atmosphere," J. Geophys. Res., 83, pp. 947-950.

Cox, R.A., and M.J. Roffey, 1977: "Thermal Decomposition of Peroxyacetyl Nitrate in the Presence of Nitric Oxide," Environ. Sci. Technol., 11, pp. 900-906.

Cox, R.A., and G.S. Tyndall, 1979: "Rate Constants for Reactions of CH_3O_2 in the Gas Phase," Chem. Phys. Lett., Vol. 65, pp. 357-360.

Cox, R.A., R.G. Derwent, and M.R. Williams, 1980: "Atmospheric Photooxidation Reactions: Rates, Reactivity, and Mechanisms for Reaction of Organic Compounds with Hydroxyl Radical," Env. Sci. and Tech., Vol. 14, pp. 57-61.

Cronn, D.R., and E. Robinson, 1979: "Vertical Profiles of Ethane and Acetylene," Geophys. Res. Lett., 6, pp. 641-644.

Crutzen, P.J., 1979: "The Role of NO and NO_2 in the Chemistry of the Troposphere and the Stratosphere," Ann. Rev. Earth Planet Sci., 7, pp. 443-472.

Ehhalt, D.H., and A. Tönnissen, 1980: "Hydrogen and Carbon Compounds in the Stratosphere," Proceedings of the NATO Advanced Study Institute on Atmospheric Ozone: Its Variation and Human Influences, Report FAA-EE-80-20, pp. 129-151.

Greiner, N.R., 1970: "Hydroxyl Radical Kinetics by Kinetic Spectroscopy: V. Reactions with Alkanes in the Range 300-500K," J. Chem. Phys., 53, pp. 1070-1076.

Hanst, P.L., 1981: "Nonmethane Organic Compounds in the Atmosphere and Their Role in the Scavenging of Stratospheric Chlorine Atoms," Preprint, U.S. Environmental Protection Agency.

Hanst, P.L., and B.W. Gay, Jr., 1977: "Photochemical Reactions Among Formaldehyde, Chlorine, and Nitrogen Dioxide in Air," Environ. Sci. Technol., 11, pp. 1105-1109.

Hanst, P.L., J.W. Spence, and E.O. Edney, 1980: "Carbon Monoxide Production in Photooxidation of Organic Molecules in the Air," Atmos. Environ., 14, pp. 1077-1088.

Hendry, D.G., and R.A. Kenley, 1977: "Generation of Peroxyradicals from Peroxy Nitrates (RO_2NO_2). Decomposition of Peroxyacetyl Nitrate," J. Amer. Chem. Soc., 99, pp. 3198-3199.

Hendry, D.G., A.C. Baldwin, and D.M. Golen, 1980: "Computer Modeling of Simulated Photochemical Smog," EPA 600/3-80-029, Final Report prepared for U.S. EPA by SRI International, Menlo Park, California.

Hudson, R.D., and E.I. Reed, 1979: "The Stratosphere: Present and Future," NASA Reference Publication 1049.

Kley, D., J.W. Drummon, M. McFarland, and S.C. Liu, 1980: "Tropospheric Profiles of NO_x," J. Geophys. Res. (in press).

Levy, H., II, 1974: "Photochemistry of the Troposphere," Adsv. Photochem., Vol. 9, pp. 5325-5332.

Lewis, R.S., et al., 1980: "Temperature-Dependent Rate Constants for the Reaction of Ground-State Chlorine with Simple Alkanes," J. Phys. Chem., Vol. 84, pp. 2009-2015.

Liu, S.C., 1981: Private communication, NOAA, Boulder, Colorado.

Manning, R., and M.J. Kurylo, 1977: "Flash Photolysis Resonance Investigation of the Temperature Dependence of the Reaction of Cl (^2P) Atoms with CH_4, CH_3Cl, CH_3F, CH_3F^+, and C_2H_6," J. Phys. Chem., 81, pp. 291-296.

Penkett, S.A., N.J.D. Prosser, R.A. Rasmussen, and M.A.K. Khalil, 1981: "Atmospheric Measurements of CF_4 and Other Fluorocarbons Containing CF_3 Grouping," (unpublished manuscript).

Rasmussen, R.A., M.A.K. Khalil, S.A. Penkett, and N.J.D. Prosser, 1980: "$CHCOF_2$(F-22) in the Earth's Atmosphere," Geophy. Res. Lett., 1, pp. 729-859.

Rudolph, J., D.H. Ehhalt, and G. Gravenhorst, 1979: "Recent Measurements of Light Hydrocarbons in Remote Areas," Proceedings of the First European Symposiumon Physio-Chemical Behavior of Atmospheric Pollutants, ISPRA, October 16-18, Commission of the European Communities, pp. 41-51.

Rudolph, J., D.H. Ehhalt, and A. Tönnissen, 1980: "Vertical Profiles of Ethane and Propane," J. Geophys. Res. (submitted).

Singh, H.B., 1977: "Atmospheric Halocarbons: Evidence in Favor of Reduced Average Hydroxyl Radical Concentration in the Troposphere," Geophys. Res. Lett., Vol. 4, pp. 101-104.

Singh, H.B., L.I. Salas, and L.A. Cavanagh, 1977: "Distribution, Sources, and Sinks of Atmospheric Halogenated Compounds," J. Air Poll. Control. Assoc., 27, pp. 332-376.

Singh, H.B., L.I. Salas, H. Shigeishi, A.J. Smith, E. Scribner, and L.A. Cavanagh, 1979a: "Atmospheric Distributions, Sources, and Sinks of Selected Halocarbons, Hydrocarbons, SF_6, and N_2O," Final Report, Grant 8038020, SRI Project 4487, EPA-600/3-79-107, SRI International, Menlo Park, California.

Singh, H.B., L.J. Salas, H. Shigeishi, and E. Scribner, 1979b: "Atmospheric Halocarbon, Hydrocarbons, and Sulfur Hexafluoride: Global Distributions, Sources, and Sinks," Science, 203, pp. 899-903.

Singh, H.B., J.R. Martinez, D.C. Hendry, R.J. Jaffe, and W.B. Johnson, 1979c: "Estimates of the Oxidant-Forming Potential of Light-Saturated Hydrocarbons," API Publication 4300, Contract API-LSHC-1977, Final Report prepared for the American Petroleum Institute by SRI International, Menlo Park, California.

Singh, H.B., L.J. Salas, A. Smith, R. Stiles, and H. Shigeishi, 1980: "Atmospheric Measurements of Selected Hazardous Organic Chemicals," Interim Report, Grant 805990, SRI Project 7774, SRI International, Menlo Park, California.

Steif, L.J., et al., 1980: "Rate Constant for the Reaction of the Hydroxyl Radical with Formaldehyde over the Temperature Range 228-362K," J. Chem. Phys., Vol. 5, pp. 2254-2258.

Stephens, E.G., 1969: "The Formation, Reactions, and Properties of Peroxyacetyl Nitrates (PANs) in Photochemical Air Pollution," Advances in Env. Sci., 1, pp. 119-146.

Trotman-Dickenson, A.F., and G.S. Milne, 1967: Tables of Bimolecular Gas Reactions, NSRDS-NBS 9, 1967.

Weiss, R.F., 1981: "The Temporal and Spatial Distribution of Tropospheric Nitrous Oxide," J. Geophys. Res. (submitted).

Williams, W.J., J.J. Kosters, A. Goldman, and D.G. Murcray, 1976: "Measurements of Stratospheric Halocarbon Distributions Using Infrared Techniques," Geophys. Res. Lett., 3, pp. 379-382.

Winer, A.M., A.C. Lloyd, K.R. Darnall, R. Atkinson, and J.N. Pitts, Jr., 1977: "Rate Constants for the Reaction of OH Radicals with n-Propyl Acetate, Sec-Butyl Acetate, Tetrahydrofuran, and Peroxyacetyl Nitrate," Chem Phys. Lett., 51, pp. 221-226.